



DEVELOPMENT OF A SCREENING MODEL FOR DESIGN  
AND COSTING OF AN INNOVATIVE TAILORED  
GRANULAR ACTIVATED CARBON TECHNOLOGY TO  
TREAT PERCHLORATE-CONTAMINATED WATER

THESIS

William C. Powell, Captain, USAF

AFIT/GEM/ENV/07-M12

DEPARTMENT OF THE AIR FORCE  
AIR UNIVERSITY

***AIR FORCE INSTITUTE OF TECHNOLOGY***

---

Wright-Patterson Air Force Base, Ohio

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William C. Powell, BSCE

Captain, USAF

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William C. Powell, BSCE  
Captain, USAF

Approved:

//SIGNED//  
Mark N. Goltz (Chairman)

13 March 2007  
date

//SIGNED//  
Fred S. Cannon (Member)

13 March 2007  
date

//SIGNED//  
Alfred E. Thal, Jr. (Member)

13 March 2007  
date

## **Abstract**

Perchlorate contamination of drinking water is a problem that has recently gained national attention. The purpose of this research was to develop a tool to predict the cost and performance of tailored granular activated carbon (T-GAC), an innovative technology to treat perchlorate-contaminated water. The ability to predict cost and performance is essential to promote transfer and commercialization of innovative technologies.

This study investigated how data obtained from small-scale laboratory tests could be applied to predict cost and performance of a full-scale T-GAC system to treat perchlorate-contaminated water. A technology model was developed using GAC design principles and using a multi-component Freundlich isotherm to describe sorption of perchlorate on T-GAC, in the presence of competing anions. Data from laboratory column experiments were used to obtain model parameters. Cost data used in the model were based on conventional GAC installations, as modified to account for the benefits of T-GAC in treating perchlorate-contaminated water.

Application of the model showed that performance and cost of a T-GAC system is very sensitive to the presence of competing ions. T-GAC appears to be a viable technology to treat perchlorate-contaminated water when the perchlorate concentrations are low and competing ion concentrations are not significant.

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William C. Powell

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# Development of a Screening Model for Design and Costing of an Innovative Tailored Granular Activated Carbon Technology to Treat Perchlorate-Contaminated Water

## **I. Introduction**

### **1.1 Background**

Perchlorate is commonly used as a component of explosives and as a powerful oxidant in solid rocket fuels. The production, storage, and use of perchlorate have resulted in contamination of drinking water throughout the US, with the majority of contamination sites found in California and Texas (US GAO, 2005). When ingested, perchlorate can decrease thyroid hormone production, which is critical for normal growth and development of the central nervous system of fetuses and infants (US GAO, 2005).

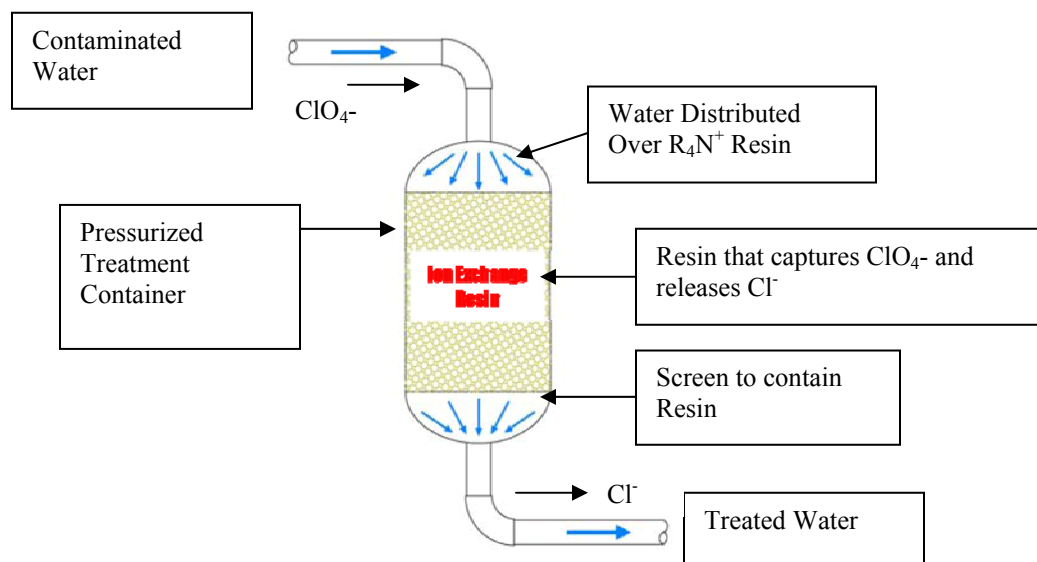
Though not currently regulated, perchlorate is on the Contaminant Candidate List and is included in the Unregulated Contaminants Monitoring Rule. In 2005, the US EPA established a reference dose of 0.0007 mg/kg/day, which is equivalent to 24.5 ppb when calculated as a Drinking Water Equivalent Level (US EPA, 2006a). US EPA is expected to set a Maximum Contaminant Level for perchlorate in the near future, and several states have already set action levels for perchlorate as low as 1 ppb (US EPA, 2006b).

Remediation of perchlorate contamination in water is difficult. It has poor adsorption qualities and biodegradation is slow. The technology that's conventionally used to treat perchlorate-contaminated water is ion exchange. This technology involves perchlorate ( $\text{ClO}_4^-$ ) exchanging with another anion such as chloride ( $\text{Cl}^-$ ) via a polymer (ion-exchange) resin consisting of a positively charged cation (e.g., a quaternary amine,  $\text{R}_4\text{N}^+$ ) with a strong affinity for perchlorate (ITRC, 2005).

Figure 1-1 shows a basic ion exchange treatment process (US Army, 2006).

Contaminated water flows through a pressurized treatment container filled with ion exchange resin, typically in the form of beads. As the water flows through the container, the perchlorate ion attaches to the resin and a chloride ion is displaced into the treated water. A screen is used to keep the beads in the pressurized container. The treated water can then be discharged safely.

Figure 1-1. Ion Exchange Treatment Process



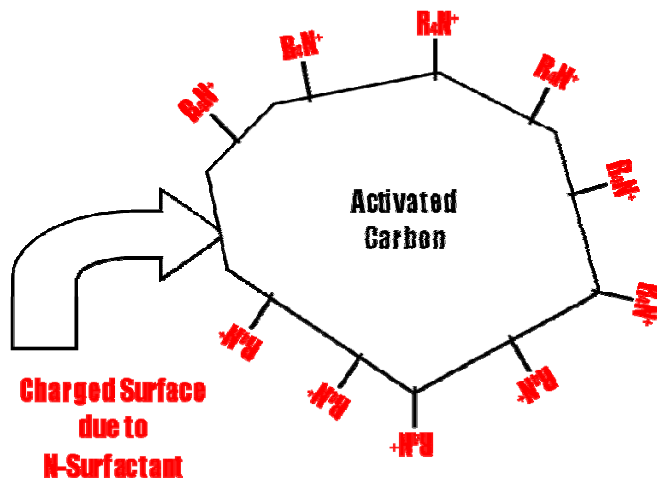
As the ion exchange resin captures perchlorate, it gives off chloride. Over time, most or all of the chloride is replaced by the perchlorate ion, and the resin is no longer effective at removing perchlorate. This is typically known as the breakthrough point. After breakthrough, the used resin must be regenerated. Unfortunately, in addition to perchlorate, the water being treated may also contain other dissolved anions, such as sulfate and nitrate. These anions can compete with perchlorate for exchange sites on the resin (ITRC, 2005; Najm et al., 1991). The presence of competing ions results in early perchlorate breakthrough and increased costs, due to the need for more frequent resin regeneration or replacement.

Although ion exchange can reduce perchlorate concentrations to acceptable levels, the main issue with the technology is cost. As noted above, when the water contains high total dissolved solids, other anions in the water compete with perchlorate for exchange sites on the resin, making treatment even more expensive and possibly cost-prohibitive (ITRC, 2005) due to the need to more frequently replace or regenerate the resin. While regeneration of the resin can offer cost savings over resin replacement, the process creates large volumes of a secondary brine waste containing perchlorate that must be further managed (ITRC, 2005; Gu et al., 2001). Fine particulates in the water can also clog the resins, which also results in more frequent replacement or regeneration of the resin. Additionally, ion exchange is not effective at removing volatile organic chemicals (VOC) such as trichloroethylene (TCE) which are often present in perchlorate-contaminated waters, and is thus not very versatile. For these reasons, the effectiveness of other technologies in treating perchlorate-contaminated water has been investigated.

As an alternative to ion exchange resins, Penn State University (PSU) has developed a tailored granular activated carbon (T-GAC) technology that can effectively remove perchlorate from water (Parette et al., 2005b). The process pre-treats granular activated carbon (GAC) with a cationic surfactant (tailoring agent), also known as an N-surfactant. The surfactant consists of a positively charged head (e.g. quarternary ammonium or pyridinium) that attracts the negatively charged perchlorate ion, and an uncharged organic tail (an alkyl chain) that is attracted to the uncharged GAC. The hydrophilic, positively charged heads (i.e.,  $R_4N^+$ ) face away from the uncharged surface (see Fig 1-2) and readily attract dissolved perchlorate anions. The uncharged carbon surface has now become a positively charged matrix which attracts the negatively charged perchlorate ion. This process is discussed more thoroughly in Chapter 2.



Figure 1-2. Simplified cationic surfactant/T-GAC configuration



Cationic surfactants are loaded onto GAC by pumping a heated and concentrated surfactant-water solution through a bed containing GAC. Heating the surfactant increases its solubility and facilitates the tailoring process. The solution is cyclically pumped through the GAC bed multiple times (ESTCP, 2005) until the surfactant is sufficiently sorbed onto the GAC.

PSU has conducted Rapid Small Scale Column Tests (RSSCT) to evaluate the performance of T-GAC to effectively treat perchlorate-contaminated water. The RSSCT is essentially a scaled-down economical version of a full-scale T-GAC system that obtains results within a short period of time as opposed to a long-term pilot or field study. Crittenden et al. (1991) pioneered the use of RSSCTs to predict GAC performance in water treatment, and their findings are the basis behind the T-GAC tests conducted by PSU. Crittenden et al. (1991) used RSSCTs to accurately predict pilot-scale treatment of groundwater and surface water contaminated with synthetic organic chemicals and

dissolved organic carbon, and developed scaling equations that will be discussed in more detail in Chapter 2. Others (e.g. Cummings et al., 1994) have also used RSSCTs and these scaling relations to effectively predict field-scale behavior of GAC for controlling disinfection by-product (DBP) formation.

The RSSCT tests conducted by PSU utilized GAC tailored with several different types of cationic surfactants to treat groundwater contaminated with perchlorate at levels ranging from 6 to 100 ppb (Parette et al., 2005b). T-GAC has also been found to effectively remove VOCs along with perchlorate, making this procedure more attractive than ion exchange (Chen et al., 2005a). Another advantage of T-GAC is that most water treatment facilities are already familiar with the use of GAC as opposed to other methods of treatment, which should accelerate acceptance of the technology. T-GAC can also be thermally reactivated (Chen et al., 2005b), prolonging its use and reducing costs when compared to ion exchange. The thermal regeneration process destroys the perchlorate ion while preserving the main surface characteristics of the T-GAC. As noted earlier, the conventionally-used ion exchange regeneration process results in a large volume of perchlorate-contaminated brine which must be subsequently managed. Therefore, the thermal reactivation of the T-GAC offers a potential costs savings versus ion exchange technology, something that's evaluated in this thesis.

There is currently an ongoing DoD Environmental Security Technology Certification Program (ESTCP) research project that investigates the effectiveness of T-GAC to treat perchlorate-contaminated water (ESTCP, 2005). As part of the project, PSU is scaling up

RSSCT data from perchlorate-contaminated water samples taken from Redlands, CA, to develop the initial design for the ESTCP study. PSU is also using perchlorate-contaminated groundwater from eastern Massachusetts in their RSSCTs to understand the impact of the differences in groundwater chemistry on the effectiveness of T-GAC in perchlorate removal. The ESTCP field pilot-scale demonstration is located at the Fontana Water Company and consists of two treatment systems. One system uses traditional GAC treatment as a control to remove perchlorate, while the other system uses the T-GAC treatment. Removal of trichloroethylene (TCE), a VOC, which is a co-contaminant in the Fontana water, will also be monitored.

## **1.2 Problem Statement**

One major hurdle faced by new technologies is during their transition from full-scale testing to commercial acceptance and integration. Often, innovative technologies which have been proven to work at full-scale fail to achieve commercial success despite their capabilities and cost-effectiveness (Mandalas et al., 1998a). Project managers, consultants, designers, regulators, etc., may be unaware of the advantages and potential of these new technologies. One way of addressing this problem is to develop tools that may be easily applied to evaluate the applicability of new technologies, in order to enable designers and stakeholders to make better-informed decisions. By developing a model that predicts both cost and performance of a T-GAC installation, the feasibility of T-GAC as a solution to particular water quality problems can be evaluated by developers and designers of treatment systems, thereby encouraging technology transfer into the commercial market.

### **1.3 Department of Defense and Air Force Relevance**

Many Department of Defense (DoD) sites face perchlorate contamination of their surface runoff and groundwater. This contaminated water may impact surrounding communities' water supplies. As a result, the DoD could be held liable for any perchlorate-related clean-up or remediation costs. The US EPA has estimated that 90 percent of all perchlorate produced in the US is for the military (US GAO, 2005). As noted above, ion exchange, which has significant costs associated with it, is the conventional method used to treat perchlorate-contaminated water

As of Jan 26, 2006, DoD policy has established 24 ppb as the level of concern for managing perchlorate (USD, 2006). DoD components must perform a risk assessment on areas of concern, and conduct follow-on actions if necessary. Additionally, the United States General Accounting Office (US GAO) has identified a need for DoD to develop an accurate and consistent cost estimating methodology regarding perchlorate remediation and clean-up (US GAO, 2004). The model developed by this thesis should help address this need with respect to perchlorate contamination in water by helping to evaluate the appropriateness of the T-GAC technology solution.

### **1.4 Definition of Terms**

Perchlorate ( $\text{ClO}_4^-$ ) - Primary chemical ingredient used in the manufacture of solid rocket propellant, as well as fireworks, flares, and commercial explosives. When ingested, it

can affect the human thyroid and cause abnormal growth and development of the central nervous system in children and fetuses (ITRC, 2005).

Ion Exchange - Conventional technology used to treat perchlorate-contaminated water. It uses a polymer resin that participates in an ion exchange reaction with perchlorate (ITRC, 2005), (see Fig 1-1).

T-GAC - Granulated activated carbon (GAC) pre-treated with alkyl quaternary ammonium or other N-surfactant for purposes of perchlorate removal (Parette et al., 2005a) (see Fig 2-1).

N-Surfactant - Surfactant that consists of a charged head containing Nitrogen and an uncharged tail (such as an alkyl chain) and a charged head (such as quaternary ammonium) that, when loaded as a cationic surfactant onto GAC, creates a positively-charged surface that attracts and captures the perchlorate anion (see Fig 1-2).

Technology Transfer - Transferring new technologies developed for one organization or environment into another (NTTC, 2006). In this case, the technology is developed in a university laboratory for commercial adoption and application in remediating perchlorate contamination at DoD sites.

## **1.5 Research Objectives**

As noted above, there is a need for a tool to make it easy for designers and stakeholders to evaluate the appropriateness of new technologies to foster their commercialization. Additionally, the US GAO has identified a need for consistent cost-estimation of perchlorate remediation. The main objective of this research is to investigate how data obtained from a small scale RSSCT can be applied to predict cost and performance, as well as to help prepare an initial design, of a full-scale T-GAC system to treat perchlorate-contaminated water. Sub-objectives include:

- 1) Evaluate how well model predictions, which are based upon the RSSCT data, compare with actual technology performance.
- 2) Based on model simulations of technology cost and performance, determine under what conditions T-GAC is a viable treatment technology.

## **1.6 Scope of Research**

The basis behind this thesis is to examine whether data obtained from small-scale RSSCT tests can be used to predict cost and performance of a full-scale perchlorate treatment system. To help determine the value of the RSSCT data, a design-cost screening tool for T-GAC treatment of perchlorate in the form of a user-friendly software program will be developed. This tool will be used to predict the cost and performance of the large scale systems being installed at Redlands and Fontana, CA. This screening tool can also be used by US military bases, as well as other stakeholders, to prepare an initial design and cost estimate for a T-GAC treatment system for given site conditions (influent characteristics, desired effluent characteristics, flow rate), allowing them to determine the appropriateness of the technology for their application.

## **1.7 Methodology**

In this study, we will scale-up RSSCT results to predict the performance and cost of a T-GAC system used to treat perchlorate-contaminated water. The study will include:

- 1) A detailed literature search/review, with the goals of:
  - a) Ascertaining the current “state of science” with respect to cost and performance of T-GAC to treat perchlorate-contaminated water.
  - b) Reviewing literature on current GAC design methods and determining an appropriate mathematical model to consider for application in T-GAC design.
  - c) Ascertaining how small scale lab results can be applied to predict large scale performance.
  - d) Reviewing literature on facilitating technology transfer to bring new technologies to market.
- 2) Use RSSCT T-GAC performance data, along with cost data from the literature, to develop a modeling tool to estimate cost and performance of a T-GAC system.
- 3) Use the model to predict cost and performance of full scale systems that are designed to treat waters of the same quality as the waters that were studied in the RSSCTs.
- 4) Perform sensitivity analyses for both model parameters and cost assumptions.
- 5) For different water qualities, compare T-GAC costs estimated by the modeling tool with costs of the conventional method used to treat perchlorate-

contaminated water, ion exchange. Based on this comparison, ascertain under what conditions T-GAC may be a viable treatment option.

### **1.8 Assumptions/Limitations**

The main assumption upon which much of this study is based is that RSSCT results are applicable to predict performance of a full-scale T-GAC system. While RSSCTs have been used in the past to design GAC systems, their ability to predict T-GAC performance is as yet untested (though this research will be one step in helping to evaluate the usefulness of RSSCTs for predicting T-GAC performance). Other limitations and assumptions include:

- 1) This work is based on a limited number of RSSCT tests. Thus, the ability to adequately model the impact of various water quality parameters, as well as other factors, on T-GAC system cost and performance is also limited.
- 2) Unavailability of performance and cost results from the Fontana study to compare with model predictions.
- 3) Limited information on costs of implementing a T-GAC treatment system.
- 4) The analysis assumes the traditional GAC system design process may be applied in designing T-GAC systems.



## **II. Literature Review**

### **2.1 Introduction**

This chapter provides an overview of the literature relevant to developing a design-cost screening model that may be used to facilitate implementation of tailored GAC technology to treat perchlorate-contaminated water. The chapter begins with a discussion of why such a model is needed. Then, results from laboratory and field studies of the T-GAC technology are reviewed. This is followed by a review of models that may be applied to simulate T-GAC performance, along with a review of RSSCTs, that can be used to obtain model parameters. Finally, the chapter closes with a discussion of methods that can be applied to estimate the costs of an innovative technology.

### **2.2 Research motivation**

In this section, we discuss the risks to human health posed by perchlorate in drinking water, the extent of perchlorate contamination in the U.S., and regulations relevant to perchlorate concentrations in drinking water that have been promulgated.

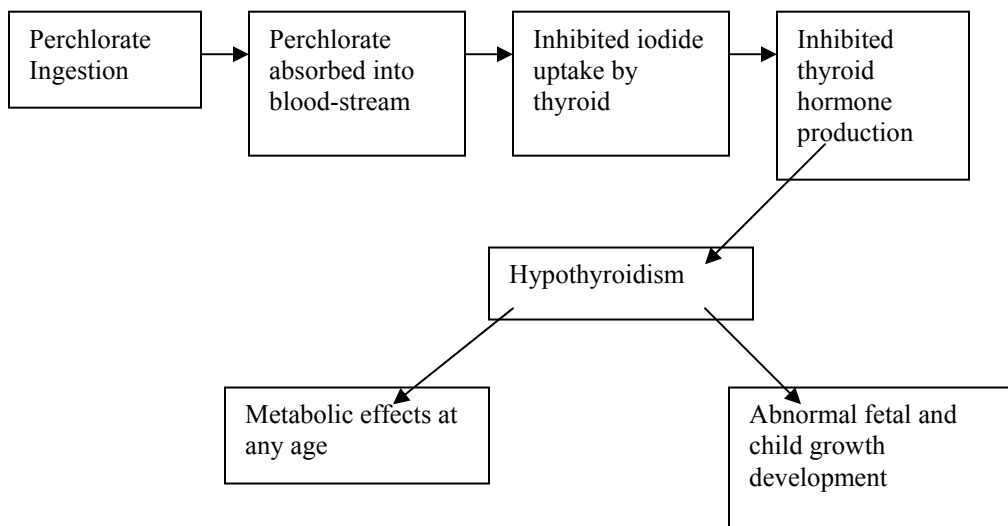
#### **2.2.1 Health effects**

Perchlorate is a concern because of the risk it poses to human health. When ingested, perchlorate can decrease thyroid hormone production, which is critical for normal growth and development of the central nervous system of fetuses and infants (US GAO, 2005).

The thyroid is a small gland at the base of the throat that uses iodide to synthesize hormones critical to the function of the central nervous system. Hypothyroidism is a condition where the thyroid makes insufficient amounts of these hormones with varying health effects, including impaired behavior, speech, and intelligence. During pregnancy,

excess stress is placed on the thyroid which, if unable to maintain an adequate level of hormones, could cause irreversible alterations in fetal neurological development (Glinoe et al., 1992). Ingesting perchlorate in significant amounts can inhibit iodide uptake by the thyroid, which resultantly can inhibit the production of thyroid hormones, with pregnant females being the most at-risk (see Fig 2-1). The Interstate Technology Research Council (ITRC, 2005) concluded that “the sensitive receptor of concern for perchlorate exposure is the developing fetus in a mother who is hypothyroid.”

Figure 2-1: Perchlorate Inhibition of Thyroid Hormone Production. Adapted from ITRC (2005)



### **2.2.2 Occurrence**

Perchlorate is a strong oxidizer, and as such, it is commonly used as a component of explosives and as a powerful oxidant in solid rocket fuels. The production, storage, and use of perchlorate have resulted in contamination of drinking water, both surface and ground, throughout the US, with the majority of contamination sites found in California and Texas (US EPA, 2005a; US GAO, 2005). Perchlorate is of particular importance to

the DoD. As perchlorate is commonly found in munitions and solid rocket fuel, many DoD facilities are vulnerable to perchlorate contamination. The US EPA has identified many sites contaminated with perchlorate. As shown in Fig 2-2, the EPA has documented contamination in 35 states, including 27 DoD sites (US EPA, 2006b). The US GAO (2004) surveyed the sampling results conducted at several contaminated DoD sites which found perchlorate contamination in groundwater at levels of up to 30,700 ppb (Table 2-1). Among EPA known perchlorate releases (US EPA, 2005a), extremely high perchlorate levels exceeded 10,000 ppb in some surface waters, and over 100,000 ppb in some groundwaters. Many DoD facilities (as well as private sites) with perchlorate contamination have impacted both groundwater and surface water sources, including some drinking water supplies (US EPA, 2005a).

Figure 2-2: Perchlorate Contaminated Sites in the U.S. (US EPA, 2006b)

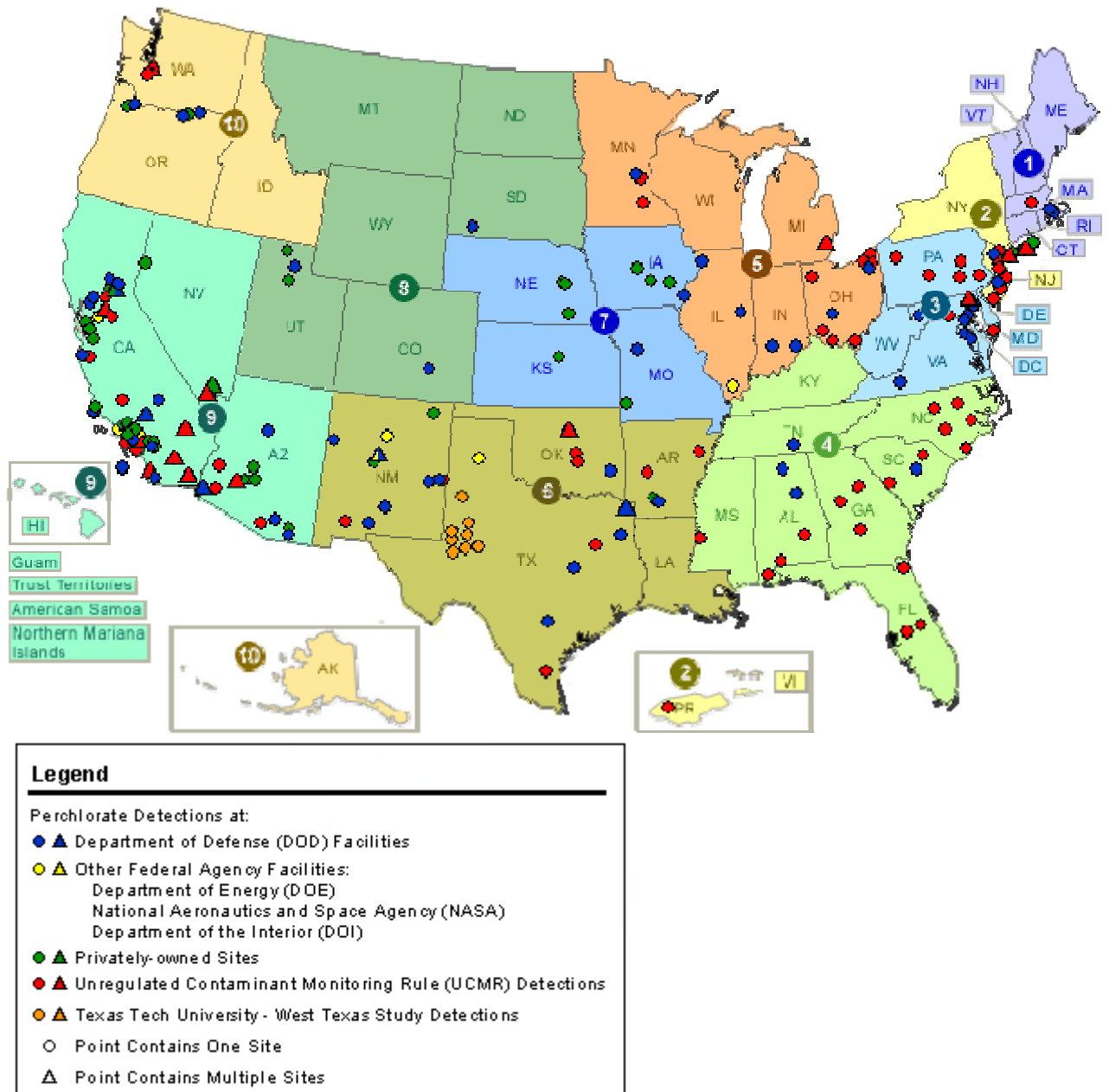


Table 2-1. Summary of Perchlorate Sampling Conducted at DoD Installations (US GAO, 2005)

<b>Installation</b>	<b>Military Service</b>	<b>State</b>	<b>Range of Concentrations Detected, ppb</b>	<b>Source of Contamination</b>
Edwards AFB	Air Force	California	up to 30,700 in groundwater	Propulsion research and rocket test stand
Holloman AFB	Air Force	New Mexico	7,600	R & D, testing and evaluation
Aberdeen Proving Grounds	Army	Maryland	< 1 to 12,000	Training with pyrotechnics and smoke; use of propellants, ordinance, smoke and chemical agents
Redstone Arsenal	Army	Alabama	up to 37,000	Rocket testing
White Sands Missile Range	Army	New Mexico	not reported	not reported
China Lake Naval Air Weapons Station	Navy	California	up to 720	R & D and testing; disposal; possible natural occurrence
Indian Head Naval Surface Warfare Center	Navy	Maryland	up to 480,000	Disposal, open burning, unknown source

### **2.2.3 Regulations**

As a result of the health effects and widespread occurrence of perchlorate contamination, the EPA has adopted a reference dose (RfD) of 24.5 ppb Drinking Water Equivalent level (DWEL) based on the National Academy of Sciences National Research Council (NRC) January 2005 report “Health Implications of Perchlorate Ingestion” (NRC, 2005; US EPA, 2006a). Based on this DWEL, DoD has established 24 ppb as the level of concern, but stated it must also comply with the more stringent of established state or federal standards (USD, 2006). When perchlorate concentrations exceed the established level of concern (24 ppb), the responsible DoD component must evaluate the extent of actual or potential exposure by conducting site-specific risk assessments. If a risk assessment

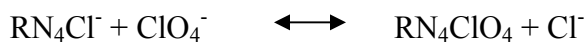
indicates that perchlorate contamination may result in adverse health effects, the responsible DoD component must prioritize the site for appropriate risk management (USD, 2006). Table 2-2 shows the current state drinking water standards that DoD must comply with, with a maximum contaminant level (MCL) as low as 2 ppb in Massachusetts.

Table 2-2. State Perchlorate Regulatory Levels as of 4/20/05 (US EPA, 2006b)

<b><u>State</u></b>	<b><u>Perchlorate Level</u></b>
Arizona	14 ppb Health Based Guidance
California	6 ppb Public Health Goal
Maryland	1 ppb Advisory Level
Massachusetts	2 ppb Maximum Contaminant Level
Nevada	18 ppb Public Notice Standard
New Mexico	1 ppb Drinking Water Screening Level
New York	5 ppb Drinking Water Planning Level
Texas	17 ppb Residential Protective Cleanup Level

#### **2.2.4 Conventional technologies to treat perchlorate-contaminated drinking water**

The technology that's conventionally used to treat perchlorate-contaminated water is ion exchange, as discussed in Chapter 1. The ion exchange process involves perchlorate ( $\text{ClO}_4^-$ ) exchanging with another anion such as chloride ( $\text{Cl}^-$ ) using a polymer (ion-exchange) resin consisting of a positively charged cation (e.g., a quaternary amine,  $\text{R}_4\text{N}^+$ ) with a strong affinity for perchlorate (ITRC, 2005) via the following reaction:



The main problem with ion exchange is cost, largely related to the need for frequent resin maintenance because of the presence of other anions in the water which compete with perchlorate for ion exchange sites (ITRC, 2005). Resin maintenance can include resin

regeneration, and subsequent brine management, or resin disposal and replacement with new resin, whichever is more economical. The pH of the water can potentially reduce the length of time the resin is effective, as can high levels of suspended solids which cause clogging of the resin (AFCEE, 2002). High operational and waste disposal costs and lower effectiveness at low perchlorate concentrations are further disadvantages of using IX to treat perchlorate (ORNL, 2007). The costs associated with the La Puente, CA, system, an extremely large IX treatment system, included operational costs of \$150 per acre-foot, brine disposal costs of \$7 per acre-foot, and capital costs of \$5M in 1999 (AFCEE, 2002). The desire to develop lower cost treatment options has spurred research into other perchlorate treatment technologies.

## **2.3 T-GAC to treat perchlorate-contaminated groundwater**

### **2.3.1 Introduction**

GAC is a widely accepted drinking water treatment technology. GAC treatment has been identified by the EPA as the best available technology (Faust and Aly, 1998) for a wide variety of contaminants, including many pesticides, synthetic organic compounds (SOC), and dissolved organic carbon (DOC). The removal of inorganic constituents in water is generally accomplished by surface reactions, complexation, and ion exchange, while organic removal is accomplished through physical adsorption. Some typical GAC treatment system configurations include gravity feed contactors, pressure contactors, and fluidized-bed contactors (MWH, 2005).

Granular Activated Carbon systems are already installed in many water treatment systems around the US for the removal of VOCs such as TCE. Studies have shown that GAC has the potential to remove perchlorate, but not efficiently (Chen et al., 2005a). Since many GAC systems are already installed at water treatment facilities, it becomes attractive to somehow modify the GAC so that it is effective at removing perchlorate in conjunction with VOCs.

Penn State University (PSU) has used RSSCTs to study how tailoring GAC with surfactants might be a means to effectively treat perchlorate-contaminated drinking water (Chen et al., 2005a). In the following sections, we discuss how T-GAC works to remove anions such as perchlorate, and then report the results of laboratory and field studies that have used T-GAC to treat perchlorate-contaminated water.

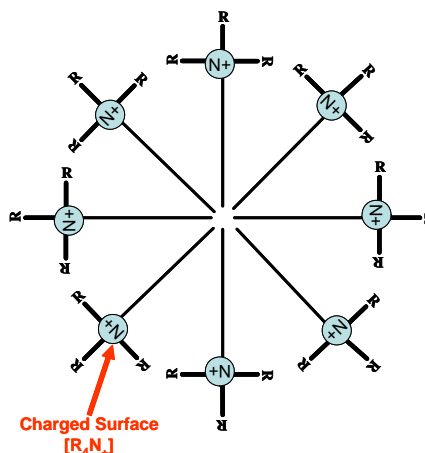
### **2.3.2 How T-GAC works**

T-GAC works similarly to GAC, only it uses a surfactant to attract the perchlorate ion (Parette et al., 2005a). As mentioned in Chapter 1, the T-GAC process pre-treats GAC with an N-surfactant that creates a charged surface and attracts the perchlorate ion. The surface of the GAC itself is uncharged (and thus, hydrophobic) and tends to repel ions such as perchlorate. However, this uncharged surface is ideal for loading of a cationic N-surfactant, which has an uncharged tail (an alkyl chain) that is attracted to the carbon, and a positively charged head (such as quaternary ammonium) which can attract the perchlorate anion (ESTCP, 2005). The prevailing theory is that when high concentrations of N-surfactant are loaded on the GAC, micelles form within the pores



and jagged surfaces of the carbon (ESTCP, 2005). An N-surfactant micelle is illustrated in Figure 2-3. The uncharged tails of the N-surfactant are attracted to each other, and the GAC surface, and form the core of the micelle. The positively charged heads (i.e.,  $R_4N^+$ ) face outward, and attract the perchlorate anion.

Figure 2-3. Cationic surfactant micelle



Cationic surfactants are loaded onto the GAC by pumping a heated and concentrated surfactant-water solution cyclically through a bed containing GAC. Heating the surfactant increases its solubility and facilitates the tailoring process. The solution cycles through enough times until the surfactant has been sufficiently sorbed onto the GAC.

Thermal reactivation is a proven method used to regenerate activated carbon. This process can thus, in principle, be used to regenerate T-GAC as well, hopefully at a cost less than would be incurred by replacing the exhausted T-GAC. A further benefit is that the thermal process destroys the perchlorate ion, so a potential waste stream is eliminated. When catalyzed by oxygen compounds of sodium, it was found that perchlorate starts decomposing at temperatures of 400 to 500° C (Sasnovskaya and Rosolovskii, 1996). Based on this, Chen et al. (2005a) hypothesized that perchlorate

adsorbed onto tailored GAC would decompose at thermal regeneration temperatures greater than 600° C. Laboratory tests conducted by Chen et al. (2005a) verified this hypothesis that the perchlorate would indeed break down, and also showed that by thermally regenerating the T-GAC, over 90% of the perchlorate capacity can be restored. Thermal regeneration was carried out in two steps. The first step exposed the GAC to a constant flow of nitrogen at 600° to 800° F, immediately followed by the second step of reactivation using either steam, CO<sub>2</sub>, or NH<sub>3</sub> at the same temperatures. The best results were obtained from using a CO<sub>2</sub> or NH<sub>3</sub> thermal treatment. Note that this research studied reactivation for GAC that was tailored with ammonia and nitrogen tailoring agents. Whether reactivation is feasible for the current tailoring agents used by PSU has yet to be explored. The different tailoring agents experimented with by PSU are discussed in section 2.3.3.

### **2.3.3 Laboratory studies of T-GAC**

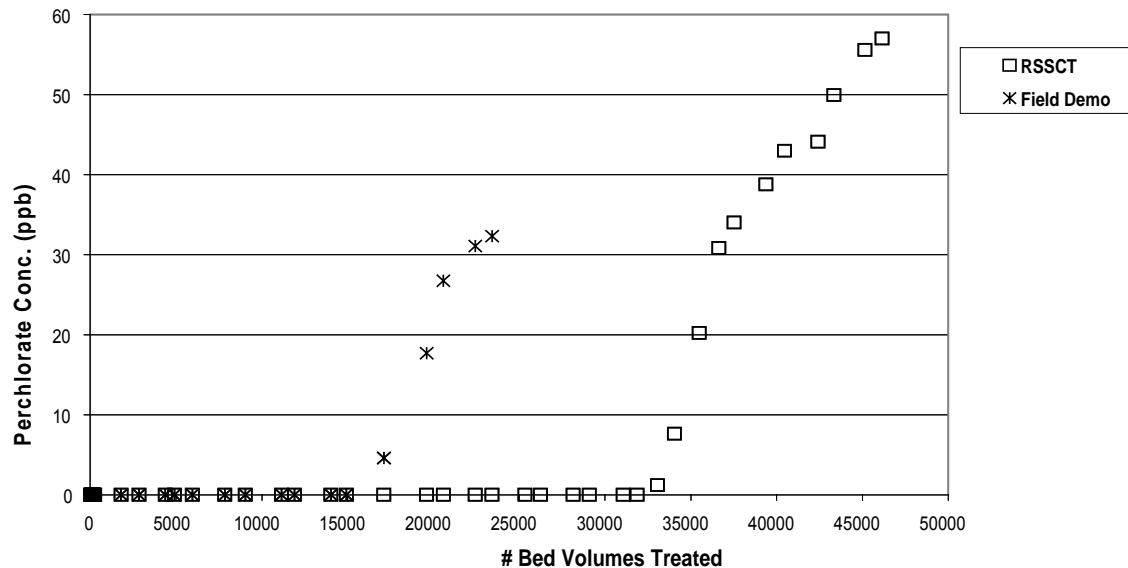
The PSU Department of Civil and Environmental Engineering has conducted all the RSSCTs with perchlorate-contaminated water used in this research. Their breakthrough curves plotting effluent perchlorate concentrations versus the number of bed volumes treated are located in Appendix A. These data are used to develop the performance model. The data are for various water chemistries tested at various empty bed contact times (EBCT). The data also include results from RSSCTs using several different tailoring agents. The tailoring agents that have been tested include cetylpyridinium chloride (CPC), cetyltrimethylammonium chloride (CTAC), Tallowalkyltrimethylammonium chloride (Arquard T-50), dicocoalkyldimethylammonium

chloride (Arquad 2C-75), decyltrimethylammonium bromide (DTAB), tributylheptylammonium bromide (THAB), and myristyltrimethylammonium bromide (MTAB) (Parette, 2005b). The tailoring agent currently used in the Fontana T-GAC demonstration is CPC (ESTCP, 2006).

#### **2.3.4 Field evaluations of T-GAC**

A field demonstration of the T-GAC technology was conducted at a water treatment plant at Redlands, CA (Cannon, 2006). In conjunction with the field demonstration, RSSCTs were conducted to see how well these tests predicted field results. The pilot-scale T-GAC system was conducted by USFilter to treat Redlands water containing 75 ppb perchlorate using two beds in series at an EBCT of 7.76 minutes each (for a total of 15.52 minutes). The T-GAC was tailored with the CPC tailoring agent. The RSSCT run was conducted by PSU on the same water and designed to mimic the pilot-scale test. Figure 2-4 compares effluent perchlorate concentration vs time observed in the field T-GAC system and an RSSCT of an equivalent, small-scale reactor.

Figure 2-4. Redland, CA Field Demonstration Results Compared to RSSCT Results (Cannon, 2006)



The results show that the field demonstration only performed half as well as the RSSCT predicted. The difference between the field demonstration results and the RSSCT results is still being investigated and has yet to be fully explained (Cannon, 2006).

### **2.3.5 Facilitating technology transfer/commercialization**

There is an identified need for performance- and cost-estimating tools to facilitate technology transfer of innovative technologies. A study by Broetzman (1997) reported that unproven, innovative technologies can drive up costs and exceed budgets if they don't perform as expected. Several laws have been enacted (e.g., Stevenson-Wydler Technology Innovation Act of 1980, Bayh-Dole Act of 1980, National Competitiveness Technology Act of 1989) to respond to the need for technology transfer by requiring

federal agencies to include and foster the use of technology transfer mechanisms. A technology transfer study on the treatment of TCE contamination conducted by Mandalas et al. (1998a; 1998b) noted the challenges and barriers to transferring a successfully demonstrated new technology, and presented an interactive cost and performance software tool to help decision makers faced with a TCE remediation problem determine if this new technology was appropriate for their particular contamination conditions.

The National Research Council (NRC, 1997) published recommendations to promote the commercialization of innovative environmental technologies. They made recommendations for technology developers to address in order to facilitate commercialization of their new technologies. Several of these recommendations dealt with reporting cost and performance data in a useful format, as summarized by Mandalas et al. (1998b) in Table 2-3 below.

Table 2-3. NRC Recommendations for Technology Developers (Mandalas et al., 1998b)

Type of Reporting	Recommendations
Performance	<p>Performance effectiveness should be reported according to the technology's ability to reduce contaminant mass, concentration, mobility, and toxicity.</p> <p>Performance data should be reported at the point of maximum effect. The location of this point in relation to the point of technology applications should be specified.</p> <p>Performance reporting should include evidence from field tests that demonstrate how the technology reduces risk.</p>
Cost	<p>Cost reporting should specify cost per unit volume of contaminated matrix treated and cost per weight of contaminant removed, treated, or contained.</p> <p>Cost reporting should specify both capital costs and operating costs.</p> <p>Cost reporting should specify assumptions about discount rate and tax benefits.</p> <p>A standardized system of "template sites" should be developed and used to compare the costs of different environmental remediation technologies.</p>

In 1995, the US EPA created the Environmental Technology Verification (ETV) program to accelerate the adoption of new technologies in the marketplace. Recently, the concept of sustainability has been introduced as part of the ETV program (US EPA, 2005b). The ETV program verifies the viability of a technology by working with developers and using real-world performance results with the goal of providing potential purchasers and regulators with an independent and credible assessment of what they are buying and permitting. As a further benefit, ETV-verified technologies are allowed to be installed in some states without additional pilot testing, thereby avoiding the associated costs of such testing (US EPA, 2005b). The ETV program identifies cost as the most important factor that guides decision-making (US EPA, 2001) by potential users. To provide clear cost information, the ETV program reports either annualized cost, the simple payback period,

or the present value (PV) cost. The overall cost estimate includes capital costs and operating and maintenance (O&M) costs, and also considers the life expectancy of the design as well as extraneous costs such as energy consumption and waste disposal. Assumptions, technical factors that impact costs, and intangible benefits and disadvantages of the technology are all reported (US EPA, 2001). The ETV reporting requirements appear to be in line with the NRC recommendations made in 1997 as summarized above in Table 2-3, and go a bit beyond by incorporating life-cycle design and intangibles.

The ESTCP is a DoD program to facilitate technology transfer of innovative environmental remediation technologies. The program funds field-scale technology demonstrations to evaluate cost, performance, and market potential in order to expedite technology transfer and implementation at DoD-owned sites (ESTCP, 2007). Cost and performance models can help address the recommendations made by the NRC by demonstrating the capabilities of a new technology, and thus “advertise” its merits and effectiveness to stakeholders. Additionally, such models can help a technology qualify for ETV-verification, an important step in gaining acceptance in the commercial market. In summary, there is a need for performance- and cost-estimating tools that are based on successful demonstrations of new and innovative technologies to facilitate their transfer. The NRC has made recommendations with respect to how cost and performance can be reported to best facilitate technology transfer (NRC, 1997). The DoD’s ESTCP and EPA’s ETV program have been established to fund technology demonstrations so that useful cost and performance data (as defined in the NRC recommendations) can be

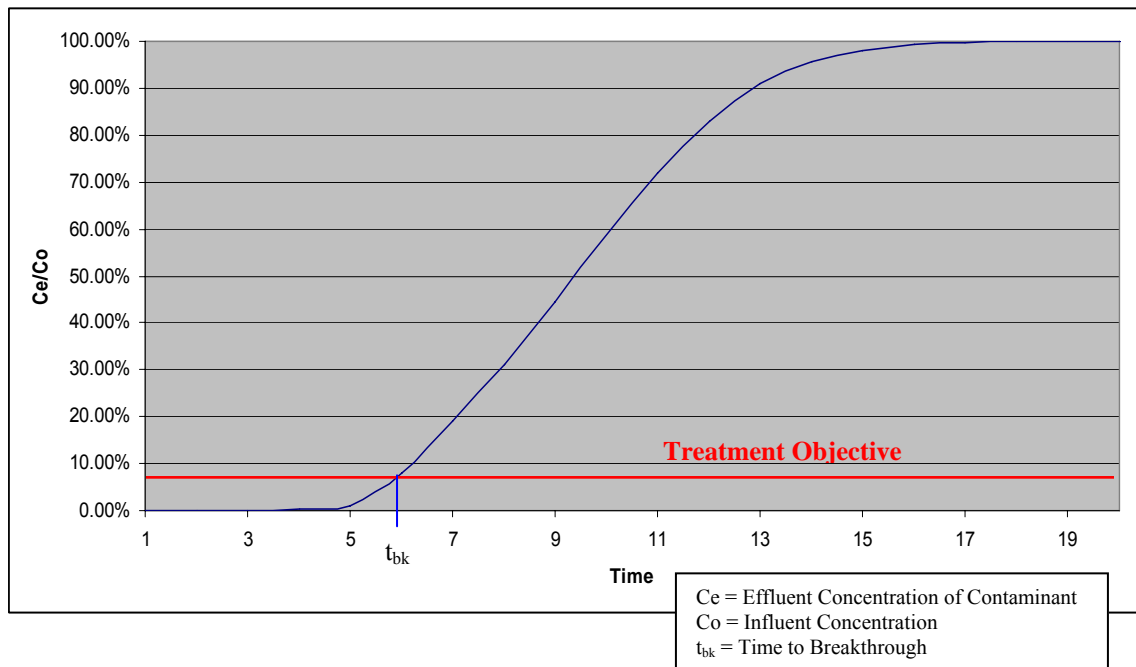
obtained to foster the commercialization of new and innovative environmental technologies.

## **2.4 Modeling T-GAC performance**

### **2.4.1 Traditional GAC Design**

As discussed above, GAC is the water treatment technology conventionally used to remove trace organic contaminants and DOC. For a typical GAC contactor with an influent concentration ( $C_0$ ) of a single contaminant, the effluent concentration-time profile (or breakthrough curve) is typically in the shape of an S-curve (Faust and Aly, 1998), as shown below in Fig 2-5.

Figure 2-5: Typical breakthrough curve for a GAC column for a single contaminant



As water passes through the GAC column, the contaminant is adsorbed by the GAC. The length of bed needed for the adsorbate (contaminant) to be transferred from the fluid



(water) to the adsorbent (GAC) is known as the mass transfer zone (Faust and Aly, 1998).

The mass transfer zone moves from the inlet of the column to the outlet, as contaminant is adsorbed. Eventually, the influent contaminant concentration at the downgradient front of the mass transfer zone appears in the effluent (see Fig 2-5). The time when the contaminant concentration exceeds the treatment objective in the effluent is known as the breakthrough time. For a single contaminant, conducting a mass balance on the mass transfer zone yields the following expression (MWH, 2005):

$$\frac{C(z)}{C_o} = \frac{q(z)}{q_e} \quad (2-1)$$

Where:  $C(z)$  = liquid contaminant concentration at location  $z$  along the mass transfer zone [ $\text{mg L}^{-1}$ ]  
 $C_o$  = influent contaminant concentration in the water [ $\text{mg L}^{-1}$ ]  
 $q(z)$  = adsorbent-phase contaminant concentration at location  $z$ ,  
( $\text{mg contaminant/g adsorbent}$ ) [ $\text{mg g}^{-1}$ ]  
 $q_e$  = adsorbent-phase contaminant concentration in equilibrium with the influent concentration [ $\text{mg g}^{-1}$ ]

The empty-bed contact time (EBCT) is the time it would take for water to flow through the empty contactor. EBCT is equal to the volume of the bed occupied by the GAC ( $V_F$ ) divided by the flow rate of the influent liquid ( $Q$ ) (MWH, 2005):

$$EBCT = \frac{V_F}{Q} = \frac{A_F L}{v A_F} = \frac{L}{v} \quad (2-2)$$

Where:  $Q$  = water flow rate through the contactor [ $\text{m}^3 \text{d}^{-1}$ ]  
 $A_F$  = cross-sectional area of contactor [ $\text{m}^2$ ]  
 $L$  = depth of media (GAC) or length of bed [ $\text{m}$ ]  
 $v$  = superficial flow velocity,  $Q/A_F$  [ $\text{m d}^{-1}$ ]

Specific throughput quantifies the performance of the GAC adsorber. Specific throughput can be defined as the volume of water that is treated by a unit mass of GAC and is expressed mathematically by (MWH, 2005):

$$\text{Specific throughput} = \frac{Qt_{bk}}{M_{GAC}} = \frac{V_F t_{bk}}{EBCT M_{GAC}} = \frac{V_F t_{bk}}{EBCT \rho_F V_F} = \frac{t_{bk}}{EBCT \rho_F} \quad (2-3)$$

Where:  
 $t_{bk}$  = time to breakthrough, days [d]  
 $M_{GAC}$  = mass of GAC [g]  
 $\rho_F$  = absorber/bed density, =  $M_{GAC}/V_F$  [g L<sup>-1</sup>]  
 Specific throughput in [L H<sub>2</sub>O g<sup>-1</sup> GAC]

Carbon usage rate (CUR) is another common parameter used to quantify the performance of a GAC adsorber. CUR is the reciprocal of specific throughput and it quantifies the mass of GAC required to treat a unit volume of water (Faust and Aly, 1998).

Design of GAC systems is commonly based on pilot studies. Designs based on pilot tests are very reliable; however, conducting such tests is relatively expensive. A more economical approach is the RSSCT, discussed later in this chapter. GAC system designs based upon parameters obtained from RSSCTs have reliably predicted full-scale performance (MWH, 2005).

Several models are used to describe adsorption in the aqueous phase. The most common are the Langmuir adsorption isotherm, the Freundlich adsorption isotherm, and Polanyi potential theory (MWH, 2005). For describing adsorption to GAC, the Langmuir isotherm is considered inferior because it is unable to account for the varying site energy of adsorption for heterogeneous adsorbents such as activated carbon. The Freundlich

isotherm does account for the varying site energies, and has thus been successfully used to describe adsorption to activated carbon (MWH, 2005). The Polanyi theory can also be used to describe the adsorption to GAC. In fact, the Freundlich parameters can be obtained by utilizing the Polanyi theory (MWH, 2005).

As the Freundlich isotherm is the most commonly used model of adsorption to GAC, and the mathematical formulation is relatively simple, this study's models will be based on the assumption of equilibrium sorption described by the Freundlich isotherm. Research by Chen et al. (2005a) has shown that tailored GAC adsorption of perchlorate behaves in accordance with the Freundlich isotherm. The Freundlich adsorption isotherm equation can be expressed as:

$$q_e = K C_{eq}^{1/n} \quad (2-4)$$

Where:  $K$  = Freundlich adsorption capacity parameter, (mg/g) (L/mg)<sup>1/n</sup>  
 $C_{eq}$  = solute equilibrium concentration (mg/L)

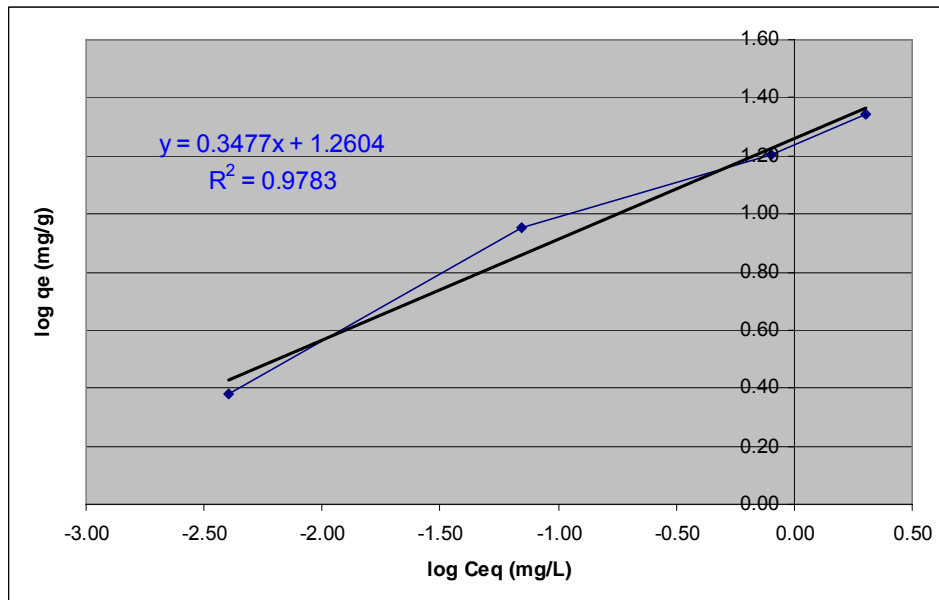
Adsorption isotherms are developed by batch tests using a fixed volume of liquid in a bottle ( $V$ ) containing a known quantity of adsorbate (such as perchlorate) at an initial concentration  $C_0$  exposed to various dosages of adsorbent (such as GAC) and stirred until equilibrium is attained (MWH, 2005). The dissolved concentration of adsorbate at equilibrium ( $C_{eq}$ ) is measured, and the adsorbent phase contaminant concentration at equilibrium ( $q_e$ ) is then calculated as (MWH, 2005):

$$q_e = \frac{V}{M} (C_0 - C_{eq}) \quad (2-5)$$

Where:  $V$  = volume of aqueous-phase added to bottle [L]  
 $M$  = mass of adsorbent [g]

A plot of  $\log q_e$  versus  $\log C_{eq}$  for various dosages of adsorbent yields a slope of  $1/n$  and an intercept of  $\log K$  as seen in Fig. 2-6. In this example,  $1/n$  is found to be 0.3477 and  $\log K$  is equal to 1.2604, found at the intercept where  $C_{eq} = 1 \text{ mg/L}$ . Chen et al. (2005a) measured  $K$ 's ranging from 17-28  $(\text{mg/g})(\text{L/mg})^{1/n}$ , and  $1/n$  values from 0.4 – 0.5 for perchlorate sorption on a number of tailored and virgin carbons. Virgin GAC had the lowest  $K$ -value.

Figure 2-6: Log plot and Linear Regression Analysis of  $q_e$  vs  $C_{eq}$ . Example of batch test results used for determination of Freundlich adsorption parameters  $K$  and  $1/n$ .



Specific throughput and GAC loading can be obtained by mass balance. Knowing that the mass of contaminant adsorbed to the GAC must equal the mass entering the contactor minus the mass leaving, the specific throughput can be estimated as follows (Faust and Aly, 1998):

$$\text{Specific throughput} = \frac{(x/m)_0}{(C_0 - C_l)} \quad (2-6)$$

Where:  $C_l$  = average effluent concentration for entire column run [ $\text{mg L}^{-1}$ ]  
(may be assumed zero if small)

$(x/m)_0$  = actual mass of a contaminant adsorbed per unit mass of adsorbent [ $\text{mg g}^{-1}$ ] when  $C_{eq} = C_0$ , and:

$$(x/m)_0 = KC_o^{1/n} \quad (2-7)$$

The Freundlich adsorption model described above is based on sorption equilibrium and the assumption that only a single compound is adsorbed onto the carbon. In reality, there are likely several compounds in the water that are also adsorbed onto the carbon. These compounds may compete for the surface sites on the activated carbon. This competition would impact how well the Freundlich isotherm, which is based upon adsorption of a single compound, predicts results when several compounds compete for sites.

Additionally, the presence of dissolved organics can impact the adsorption capacity of the carbon, as well as how fast adsorption occurs (Faust and Aly, 1998). As a result, various mathematical models have been developed to account for this behavior of mixed solutes utilizing the knowledge of the adsorptive properties of the individual components.

One such model is a Freundlich-type multi-component isotherm equation. For component  $i$  in a  $k$ -component system, the adsorbed concentration of the  $i^{th}$  component may be expressed as (Faust and Aly, 1998):

$$(x/m)_i = K_i C_i \left( \sum_{j=1}^k a_{ij} C_j \right)^{(1/n_i - 1)} \quad (2-8)$$

Where:  $a_{ij}$  = competition coefficient [dimensionless]  
 $C_j$  = contaminant  $j$  concentration [ $\text{mg L}^{-1}$ ]  
 $K_i, n_i$  = Freundlich adsorption parameters for contaminant  $i$   
 $C_i$  = contaminant  $i$  concentration [ $\text{mg L}^{-1}$ ]

$K_i$  and  $n_i$  are determined from component  $i$ 's sorption behavior in a mono-component system as described above, and  $a_{ij}$  is the competition coefficient that describes inhibition to adsorption of component  $i$  by component  $j$ .

Although the above isotherm expressions (Equations (2-4) and (2-8)) assume equilibrium between adsorbed and dissolved phases, GAC design is accomplished assuming equilibrium is not achieved (Faust and Aly, 1998). The EBCT, which is a measure of the apparent contact time between the water and the carbon, therefore impacts the performance of the GAC column. In pilot studies, as the EBCT increases, the number of bed volumes (# BVs) to breakthrough increases, where EBCT and #BVs can be determined by:

$$EBCT = \frac{V_F}{Q} = \frac{L}{v} \quad (2-9)$$

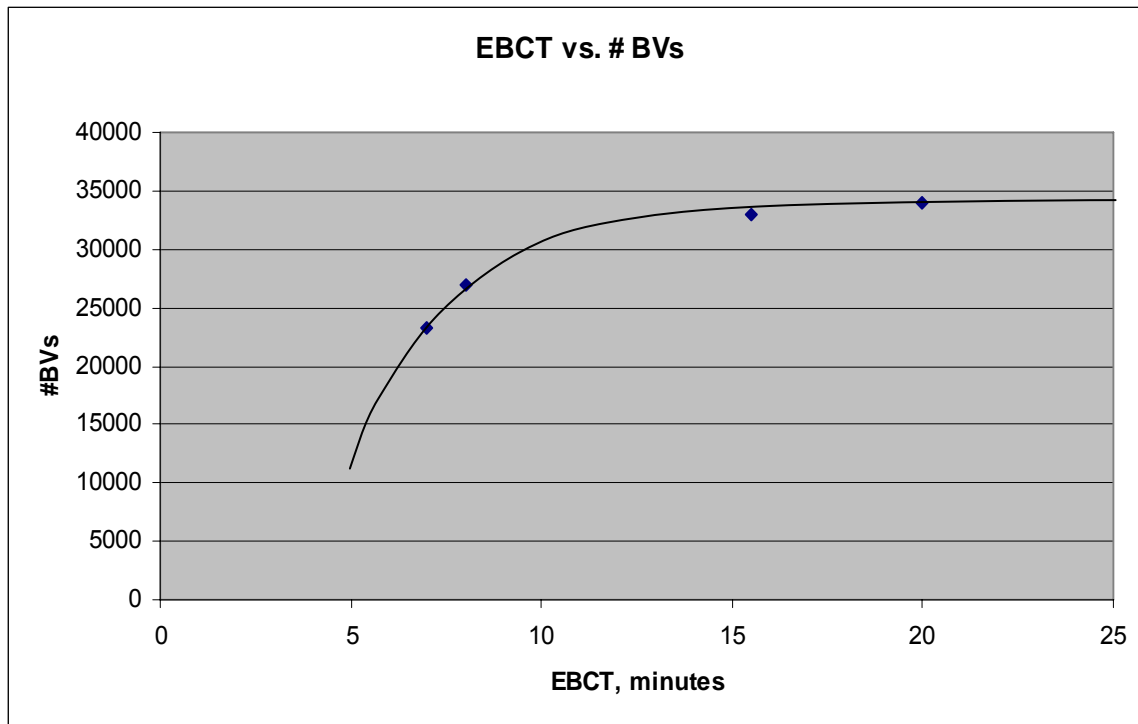
$$V_F = \frac{M_{GAC}}{\rho_F} \quad (2-10)$$

$$\#BV_S = \frac{V_{treated}}{V_F} \quad (2-11)$$

Where:  $M_{GAC}$  = weight of the GAC [g]  
 $V_{treated}$  = volume of water treated by one bed volume of GAC until breakthrough is reached [L]  
 $\#BV_S$  = number of bed volumes treated to breakthrough [dimensionless]

Figure 2-7 is a typical plot of #BVs treated versus EBCT (Faust and Aly, 1998). We see that as EBCT increases, the # BVs that can be treated increases until a maximum value is reached.

Figure 2-7: Plot of EBCT versus # BVs for Redlands RSSCT data



The way to obtain parameter values for use in a model is by inverse modeling (i.e., measuring data and finding model parameters that best fit the data). Pertinent data include breakthrough curves (effluent perchlorate concentration vs bed volumes treated) and number of bed volumes that can be treated before perchlorate breakthrough. The RSSCT method is a relatively inexpensive and easy way of obtaining the necessary data.

#### **2.4.2 Rapid Small Scale Column Test**

As noted in Chapter 1, the RSSCT is a scaled-down version of a full-scale GAC water treatment system that can be used to determine model parameter values to predict full-scale performance within a short period of time. Crittenden et al. (1986; 1991) pioneered this use of RSSCTs as a rapid method for the design of large-scale fixed-bed GAC adsorbers, and developed and tested scaling equations for designing full-scale adsorbers

based upon the results obtained from small column RSSCTs. To apply RSSCT results to simulate a large-scale adsorber, particle size (of the medium), hydraulic loading, and empty-bed contact time (EBCT) must be properly upscaled.

Crittenden et al. (1991) found that if the void fractions, bulk densities, and capacities are identical for the GAC used in both the RSSCT and full-scale process, scaling of the EBCT can be determined from:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[ \frac{d_{p,SC}}{d_{p,LC}} \right]^{2-X} = \frac{t_{SC}}{t_{LC}} \quad (2-12)$$

Where: SC = Small Column, LC = Large Column

$d_p$  = adsorbent particle size [cm]

$t$  = elapsed time in the respective column test [min]

$X$  = the dependence of the intraparticle diffusion coefficient on particle size

Crittenden et al. (1991) note that when internal diffusion controls the adsorption rate so that the intraparticle diffusivity is a linear function of particle size (referred to as proportional diffusivity),  $X = 1$  in equation (2-12). For hydraulic loading, or superficial velocity ( $v$ , cm/s), the equation that ensures proportional diffusivity, and thus  $X = 1$ , is given by (Crittenden et al, 1991):

$$\frac{v_{SC}}{v_{LC}} = \left[ \frac{d_{p,LC}}{d_{p,SC}} \right] * \frac{Re_{SC \min}}{Re_{LC}} \quad (2-13)$$

and  $Re_{SC \min}$  is the minimum  $Re$  that guarantees the effects of dispersion and external mass transfer in the small column do not exceed those of the large column. The Reynold's number is defined as (Droste, 1997):



$$\text{Re} = \left[ \frac{\rho v \psi d_p}{u} \right] \quad (2-14)$$

Where:

- $\rho$  = density of water [ $\text{g cm}^{-3}$ ]
- $v$  = superficial velocity [ $\text{cm s}^{-1}$ ]
- $u$  = viscosity of water [ $\text{g cm}^{-1} \text{s}^{-1}$ ]
- $d_p$  = media grain diameter [cm]
- $\psi$  = sphericity of filter media [unitless]

RSSCT results are used to design a full-scale system. The EBCT for the full-scale system is found by using equation 2-12, which is needed to size the system ( $V_F$ ) using equation 2-2. The time to breakthrough from the RSSCT results is recorded, annotated in equation 2-3 as  $t_{bk}$ . The operating time until breakthrough for the full-scale system ( $t_{bk}$ ) is also found using equation 2-12 where  $t_{LC}$  and  $t_{SC}$  become the times to breakthrough for the large and small column respectively, with  $t_{SC}$  obtained from the RSSCT results. Note that ( $t_{bk}/\text{EBCT}$ ) in equation 2-3 will give you the #BVs treated as calculated in equation 2-11. Specific throughput is then found using equation 2-3. Annual GAC consumption is calculated as the volume of water treated in a year divided by the specific throughput.

An alternate method for design uses equations 2-9 through 2-11. The EBCT for the full-scale system is once again found using equation 2-12 as above to determine  $V_F$  (using equation 2-9) and then the mass of GAC may be calculated using equation 2-10. In contrast to the method described above, the RSSCT results provide the #BVs to breakthrough as opposed to  $t_{bk}$ . The volume of water treated ( $V_{\text{treated}}$ ) is obtained by multiplying #BVs by one bed volume ( $V_F$ ). The length of time the system can treat water is simply the volume of water treated divided by the flow rate. .

## **2.5. Estimating Costs**

As noted above, ion exchange (IX) is the conventional technology currently used to treat perchlorate-contaminated water. Thus, estimated costs of the T-GAC technology will be compared with costs of IX to help determine the economic viability of T-GAC to treat water of a given quality at a specified flow rate.

Per a telephone conversation with Mr. Tim Peschman (2006), the Remediation Product Manager at Siemens Water Technologies Corp., the current costs for IX treatment of perchlorate is between \$125 and \$225 per acre-foot, with an average of 175,000 BVs treated before regeneration or disposal of the IX resin is required.

Mr. Peschman also described the design of a typical T-GAC system. A system consists of a number of treatment trains, each of which has two contactors, a lead contactor and a lag contactor, in series. When the GAC in the lead contactor is completely exhausted, it is disconnected from service and the water to be treated flows to the lag contactor. After servicing, the lead contactor is then placed in the lag position. The typical contactor has a diameter of 12 feet, which generally accommodates flow rates between 950 and 2400 gpm. The bed depth is varied to provide the required EBCT. For flow rates greater than 2400 gpm, multiple trains are placed in parallel to assure the flow rate per train is between 950 and 2400 gpm.

The costs associated with implementing a T-GAC filtration system include initial capital costs and operating and maintenance (O&M) costs. The main O&M costs are for power and GAC disposal or regeneration.

### **2.5.1 Initial Capital Costs**

Initial capital costs are those costs associated with installing a complete filtration system, including, but not limited to, startup costs, testing, mobilization, filter vessels, GAC media, site-specific design and construction/site preparation, labor, and ancillary equipment (tools, piping, etc.). Using vendor quotes, a study by Creek and Davidson (NWRI, 2000) found that systems over 600 gpm did not enjoy a significant economies-of-scale cost benefit. The study found that the capital costs for a 120,000 lb GAC system was \$1,019,000 and the costs for a 720,000 lb GAC system was \$5,979,000 (NWRI, 2000). Both estimates equate to approximately \$8 per lb GAC.

### **2.5.2 Operating and Maintenance Costs**

Creek and Davidson (NWRI, 2000) cite a quote from USFilter for \$1.35 per lb GAC, including change-out labor and transport costs. More recently, USFilter quoted a cost range for coal-based GAC media from \$0.80 to \$1.50 per pound, plus a service charge for labor of \$5,000 per bed (Gillen, 2007). GAC can be regenerated, although it is uncertain whether it would work with the T-GAC technology. An EPA wastewater technology fact sheet (US EPA, 2000) cited costs for regenerated GAC from \$0.50 to \$0.78 per pound, compared to normal prices for virgin GAC of \$0.70 to \$1.20 per pound at the time, illustrating a potential for savings of \$0.20 to \$0.40 per pound of GAC in

media costs. Additionally, Dr. Fred S. Cannon (2007), a professor for the Department of Civil and Environmental Engineering at PSU, stated that expected media savings from utilizing thermal regeneration of GAC are approximately \$0.30 per pound.

#### **2.5.2.1 Disposal Costs**

Spent GAC contaminated with hazardous waste is commonly disposed of at a waste-to-energy facility where it is incinerated. A study conducted by the Federal Remediation Technologies Roundtable (2007) found that costs associated with ex situ incineration of hazardous waste-contaminated soil ranged from \$40 to \$44 per cubic foot. If the GAC were to be regenerated, GAC waste, and therefore disposal costs, could be eliminated. Dr. Cannon (2007) stated that thermal destruction of GAC contaminated with perchlorate should be much cheaper than incinerating hazardous soil. The GAC is reduced to a small amount of ash, and there are no secondary toxic contaminants to manage as the perchlorate is destroyed by incineration. Additionally, significantly less fuel is needed to burn the GAC. Costs for thermal disposal of perchlorate-contaminated GAC are estimated at \$10 per cubic foot (Cannon, 2007).

#### **2.5.2.2 Power Costs**

One cost associated with the filtration system is the amount of power required to overcome headloss through the filter media. A commonly used equation for estimating headloss in a filter was developed by Ergun (1952), and is commonly written as (Droste, 1997):

$$\frac{h_L}{L} = \frac{150\mu}{\rho g} \frac{(1-e)^2}{e^3} \frac{v}{(\psi d_p)^2} + k \frac{1-e}{e^3} \frac{v^2}{\psi d_p g} \quad (2-15)$$

Where:  
 $h_L$  = head loss through media [cm]  
 $L$  = Depth of media filter [cm]  
 $e$  = porosity of filter media [unitless]  
 $\psi$  = sphericity of filter media [unitless]  
 $k = 1.75$

Headloss is an expression of how much head is needed to be overcome by water moving at a certain superficial velocity through the media. The following expression is used to calculate the power required for a specified flow rate ( $Q$ ) to overcome headloss ( $h_L$ ):

$$Power = Q_m g h_L \quad (2-16)$$

Where:  
 $h_L$  = head loss through media converted to meters [m]  
 $g$  = acceleration of gravity [ $m s^{-2}$ ]  
 $Q_m = Q\rho$  = mass flow rate [ $kg s^{-1}$ ]  
 $Power$  = [watts]

### **2.5.3 Discount Rate**

To incorporate the time-value of money in an economic analysis, the discount rate is used. The discount rate can be considered as the minimum acceptable of rate of return (Blank and Tarquin, 2005). Government agencies commonly use a discount rate to evaluate the cost of a project. The discount rate can be used to convert a cost as of today, also known as a present worth cost, into an annuity, or to convert an annuity into a present worth. The relationship between the present worth cost (PW) and an annuity (A) is shown in the equation below (Blank and Tarquin, 2005):

$$A = PW * \frac{i(1+i)^n}{(1+i)^n - 1} \quad (2-17)$$

Where:         $i$  = discount rate [%]  
                  $A$  = Annuity or Annual Worth [\$]  
                  $PW$  = Present Worth [\$]

The US Office of Management and Budget (US OMB) recommends (as of January 2007) using the real discount rate - the discount rate from which inflation has been removed – in cost-effectiveness analyses (US OMB, 2007). The recommended rates to use are 2.8% over 10 years and 3.0% over 20 and 30 years (US OMB, 2007).

### **III. Methodology**

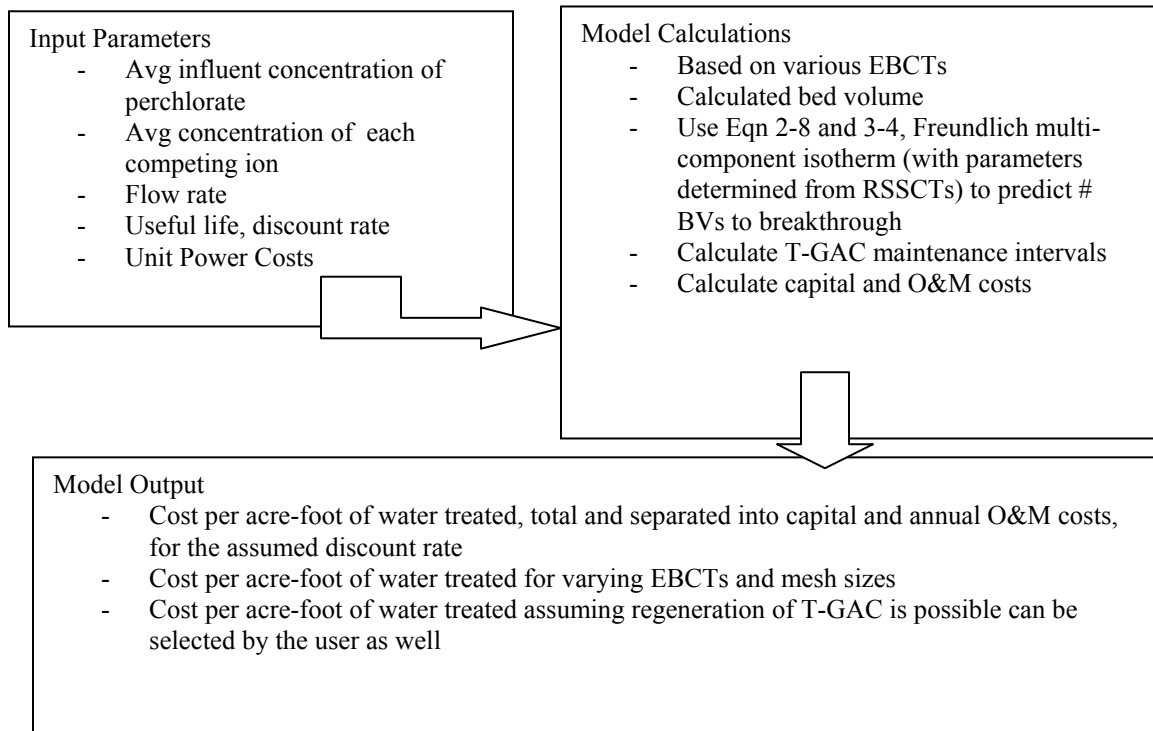
#### **3.1 Introduction**

The purpose of this chapter is to describe the method by which the design-cost screening model is developed, using RSSCT data obtained from PSU.

One of the needs for technology transfer, as mentioned in Chapter 2, is that unit treatment costs be reported. Therefore, the output of this model will be in treatment costs per acre-foot, separated into capital costs and annual operation and maintenance (O&M) costs. To estimate these costs, it will be necessary to predict the number of bed volumes that can be treated before breakthrough (#BVs), and the expected volume of T-GAC required.

Figure 3-1 conceptually lays out how user inputs of influent perchlorate and competing ion concentrations and flow rate may be used to calculate costs. Costs will be calculated assuming: (1) T-GAC must be replaced after breakthrough, and (2) T-GAC can be thermally regenerated. Details of the calculations, and how parameter values for the Freundlich multi-component isotherm are obtained from RSSCT data, are discussed in the sections below.

Figure 3-1. Model Flow Chart



### **3.2 Calculation of Parameters for Freundlich Multi-component Isotherm from RSSCT Data**

The design approach is to use RSSCT data from PSU to determine parameter values in the Freundlich multi-component isotherm equation (Equation 2-8). The decision to use a Freundlich isotherm was made because past research demonstrated that a Freundlich isotherm successfully modeled perchlorate adsorption on tailored GAC (Chen et al., 2005a). The decision to use the Freundlich multi-component isotherm was made because of its simplicity, ease of use, and the fact that its application does not require many difficult-to-measure parameters.

All RSSCT data analyzed originated from the PSU Environmental Engineering department. It is contained in the appendices. The breakthrough curves for EBCT versus



# BVs for all available RSSCT data were plotted, and an estimated # BVs to breakthrough for each was calculated, as shown in Appendix A. The water chemistry for each water is shown in Appendix B.

### **3.2.1 Determination of Freundlich Parameter K**

As discussed in Chapter 2, previous research with both virgin and tailored GAC (Chen et al., 2005a) has shown that perchlorate adsorption can be described using a Freundlich adsorption isotherm. Freundlich parameters are typically obtained using the batch test described in Section 2.4.1. Unfortunately, no data for perchlorate adsorption on the particular T-GAC being used in this study are available at this time so another way of estimating the parameters K and 1/n must be made using various assumptions. K was determined based on an RSSCT run conducted by PSU using distilled de-ionized water containing 1 mg/L of perchlorate and an EBCT of 20 minutes for an 8 x 30 mesh media grain size. By inverse-modeling and assuming the 20-minute EBCT is only sufficient to achieve an x/m value that is 95% of the equilibrium adsorbed phase contaminant concentration ( $q_e$ ), the following equation adapted from Chapter 2 (equations 2-4 to 2-7) can be used to determine K:

$$(x / m)_{ClO_4} = 95\% * q_e = 95\% * K_{ClO_4} C_{0,ClO_4}^{1/n} \quad (3-1)$$

Where (x/m) can be calculated from the RSSCT data by using the volume of water treated to determine the total amount of perchlorate adsorbed onto a single bed volume of GAC (assuming the effluent perchlorate concentration is negligible):

$$(x / m)_{ClO_4} = \frac{(\#BV\text{sTreated})(C_{0,ClO_4})[mg / L]}{\rho_F[g / L]} \quad (3-2)$$

So this is a pseudo-adsorbed phase contaminant concentration ( $q$ ), and it equals the mass of perchlorate that has been adsorbed into the bed of activated carbon when a breakthrough of 6 ppb of perchlorate has occurred. It is recognized that the true equilibrium adsorbed phase contaminant concentration ( $q_e$ ) would theoretically not be discerned until full breakthrough of perchlorate had occurred, and it would be a larger number. However, pseudo-Freundlich  $K$  and  $1/n$  values can be discerned as a function of  $q$  and  $C_0$ , just as true Freundlich  $K$  and  $1/n$  values could be discerned as a function of  $q_e$  and  $C_0$ . Moreover, the pseudo-Freundlich  $K$  and  $1/n$  values can be mathematically modeled relative to one another as a function of perchlorate concentrations and competing species concentrations, just as could the true Freundlich  $K$  and  $1/n$  values for equilibrium isotherms. Thus, for  $C_0 = 1$  (mg/L) and an EBCT of 20 minutes, the pseudo-Freundlich  $K$  is simply determined by:

$$K_{ClO_4} = (x / m)_{ClO_4} / 95\% \quad (3-3)$$

The value of the pseudo-Freundlich  $K$  obtained from the RSSCT and Equation 3-3 may be compared with typical values obtained in the past for perchlorate adsorption on GAC with other tailoring agents (Chen et al., 2005a).

### **3.2.2 Determination of Freundlich Parameter 1/n**

The parameter  $1/n$  could not be estimated from the data that were used to estimate  $K$  because estimation of  $1/n$  would require multiple RSSCTs with different perchlorate influent concentrations in distilled-deionized water. Chen et. al. (2005a) found  $1/n$

values for tailored and virgin GAC ranging from 0.4 to 0.5, so these values will be tested.

The sensitivity of the model to varying values of  $1/n$  will be ascertained.

### **3.2.3 Determination of Competition Coefficients**

The competing ions will be accounted for using the Freundlich multi-component isotherm defined in Equation 2-8. To use this equation, the competition coefficients,  $a_{ij}$ , must be determined.

An MS Excel Spreadsheet was used in combination with the Solver Excel program to determine the parameters in Equation 2-8. Assuming that equilibrium is not achieved during the RSSCTs, and that we can calculate how close we are to equilibrium by knowing the EBCT, we can modify Equation 2-8 as follows:

$$(x/m)_{ClO_4} = (\% \text{ achieved } q_e) K_{ClO_4} C_{ClO_4} \left( \sum_{j=1}^k a_{ClO_4,j} C_j \right)^{(1/n - 1)} \quad (3-4)$$

The Excel spreadsheet included the RSSCT-estimated #BVs for 11 different water chemistries, and the above formula was entered into the spreadsheet. For details on the performance model's development, see Appendix F. A brief summary follows here.

The Freundlich  $K$ - and  $1/n$  values were set as constants. The % achieved  $q_e$  for each RSSCT run's respective EBCT was determined using the chart/graph developed in section 3.3 (simulated 8 x 30 mesh). The model calculates  $x/m$  using equation 3-4, which is then used to calculate the #BVs to breakthrough. This calculated #BVs is then compared to the experimental RSSCT results, and a percentage difference between the

two values is calculated. The sum of these errors is then used as the objective function by Solver. Solver iteratively finds the competition coefficients in equation 3-4 that minimizes the objective function.

#### **3.2.4 Sensitivity Analyses**

Analyses were conducted to examine how total error, as well as the maximum single RSSCT run error, was affected by varying the different parameters. The total error is defined as the sum of the percent differences between the model-predicted and observed # BVs to breakthrough for the different RSSCT runs. The maximum single RSSCT run error is defined as the largest percent difference between the model-predicted and observed # BVs to breakthrough observed in all the RSSCT runs.

The sensitivity of the best fit competition coefficients, total error, and maximum single RSSCT run error to changes in K was determined by varying K from 20 to 35 and running Solver. Solver was also set to change both the competition coefficients and K simultaneously to determine the best-fit value of K, so it could be compared to the value of K initially determined from the literature.

The sensitivity of the best fit competition coefficients, total error, and maximum single RSSCT run error, to changes in  $1/n$  was determined by varying  $1/n$  from 0 to 0.5 and running Solver. Solver was also set to change both the competition coefficients and  $1/n$  simultaneously to determine the best-fit value of  $1/n$ , so it could be compared to the value of  $1/n$  expected from the literature review (in the range 0.4 to 0.5).

Solver was finally run with the values of  $K$ ,  $1/n$ , and the competition coefficients unconstrained. In this way, the “best” values of these parameters (defined as those values which resulted in the lowest total error) could be determined.

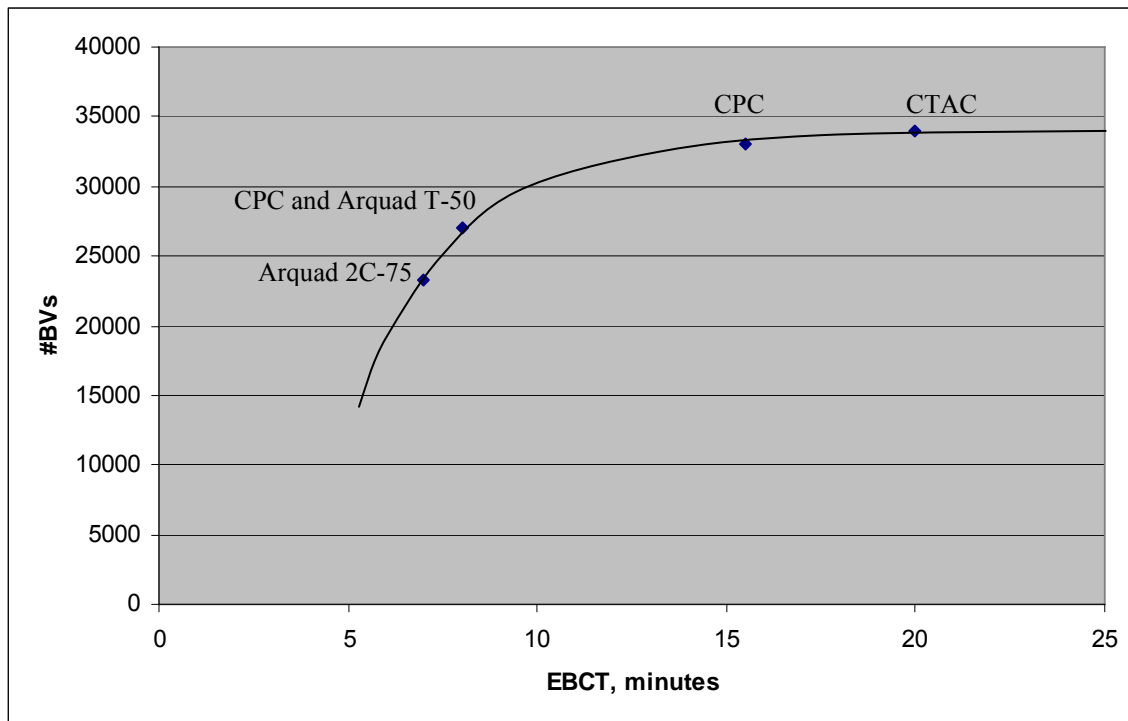
### **3.3 Design Approach**

Having obtained the Freundlich multi-component isotherm parameters from the RSSCT experiments, the parameterized model can then be used to predict the number of bed volumes to breakthrough (#BVs) for specified concentrations of perchlorate and competing ions, at a pre-determined EBCT. The EBCT determines the size and cost of the initial design, for a given flow rate, while the number of bed volumes to breakthrough may be used to determine the O&M costs associated with periodic T–GAC replacement or regeneration. A walk-through of the final design-based cost model is located in Appendix E.

#### **3.3.1 Determination of EBCT Relationship Curve**

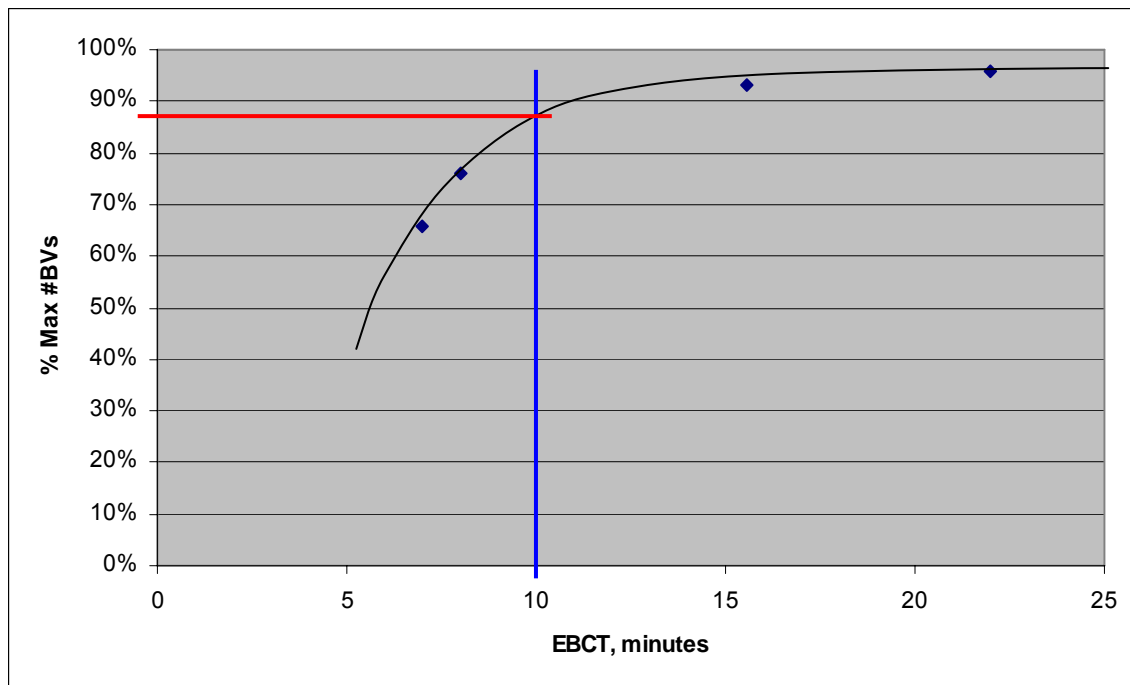
The EBCT impacts costs by dictating the size of the reactors, as well as affecting the number of bed volumes to breakthrough (#BVs) as discussed in Chapter 2. Using the Redlands data in Appendix A (simulated for an 8 x 30 mesh), a figure showing the number of bed volumes to breakthrough vs EBCT was prepared (Figure 3-2).

Figure 3-2. Plot of EBCT vs. # BVs to Breakthrough for Redlands Data from Appendix A. The tailoring agent for each RSSCT run is noted.



As can be seen from Figure 3-2, the number of bed volumes to breakthrough approaches a maximum value as discussed in Chapter 2 (see Figure 2-7). Thus, the longer the EBCT, the more water a given amount of T-GAC can treat (resulting in less operating costs needed for periodic GAC replacement or regeneration). However, as the EBCT increases, the T-GAC column size increases, and therefore, the initial capital cost of the system increases. Thus, an optimal EBCT should be selected that considers both capital costs and operating costs associated with periodic T-GAC replacement or regeneration. Assuming that at a 22-minute EBCT, the number of bed volumes to breakthrough is 96% of its maximum value, Figure 3-2 can be used to construct Figure 3-3 which shows the relationship between EBCT and percent of the maximum number of bed volumes to breakthrough.

Figure 3-3. EBCT Relationship Curve: EBCT vs. % Maximum # BVs to breakthrough



We may also assume that the relationship plotted in Figure 3-3 applies when plotting the fraction of maximum adsorbed concentration ( $x/m$ ) versus EBCT. That is, we implicitly assume that for large EBCT, sorbed concentrations approach equilibrium ( $q_e$ ) with the influent concentration ( $C_0$ ), and  $x/m$  approaches  $q_e$ . However, at smaller EBCTs, equilibrium is not attained, and the extent of early breakthrough is directly related to the extent of non-equilibrium sorption. This assumption is consistent with previous findings that equilibrium is not achieved in columns, and that equilibrium is approached as contact time increases (Faust and Aly, 1998). Using data obtained from PSU (Appendix A), and assuming the adsorbed concentration ( $x/m$ ) measured in a column with a 22-minute EBCT is 96% of the equilibrium adsorbed concentration ( $q_e$ ), Table 3-1, which relates EBCT to approach to equilibrium (measured as %  $q_e$ ), can be developed.

Table 3-1. Approach to adsorption equilibrium as a function of EBCT, using PSU data from Redlands water containing 75 ppb  $\text{ClO}_4^-$ \*. Table 3-4 shows the final tabulations for each grain size included in this research.

EBCT minutes	x/m mg/g	Achieved % $q_e$
22	5.32	96%
15.52	5.09	91%
8	4.23	75%
7	3.65	65%

\* $q_e = 5.6 \text{ mg/g}$  assuming  $5.32 \text{ mg/g}$  is 96%  $q_e$

As no data are available to determine the “optimal” EBCT, considering both capital and O&M costs, it was assumed that the optimal EBCT is 10-minutes, which we see from Figure 3-3 equates to approximately 88% of  $q_e$ . The sensitivity of system cost to EBCT will be determined.

### **3.3.2 Example Use of RSSCT Data to Design a Full-Scale T-GAC Adsorber**

As an example, a hypothetical RSSCT was performed to evaluate the removal of 50 ug/L perchlorate from a groundwater supply using adsorption on T-GAC. The RSSCT was designed to simulate a full-scale adsorber with an EBCT of 20 minutes and a flow rate of  $10^6 \text{ L/d}$  (Table 3-2). Following Crittenden et al. (1991), the RSSCT column was designed based on the full-scale adsorber parameters (Table 3-2). By conducting the RSSCT, we can determine the GAC specific throughput for a treatment objective of 1 ppb, as well as determining the annual GAC usage (kg/year) for the specified design flow of  $10^6 \text{ L/d}$  (694 L/min). Bed volume can be determined from the design flow rate and EBCT using equation 2-9.

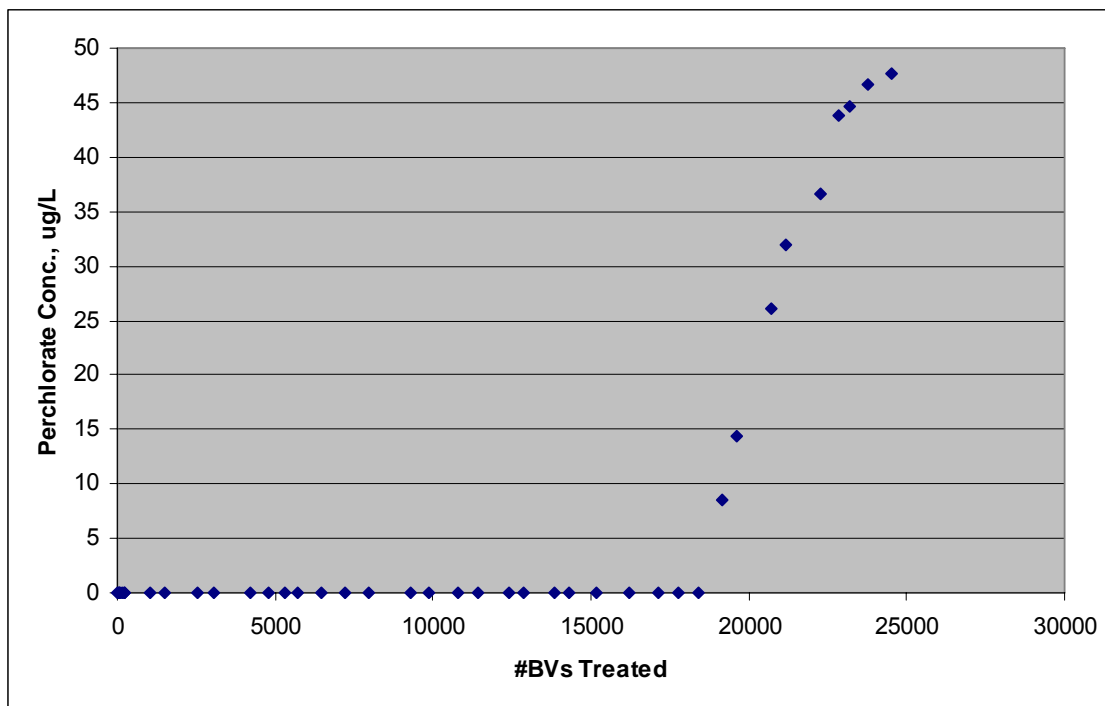


Table 3-2: RSSCT Parameters Based on Full-scale Adsorber Design

Item	Unit	Full-Scale Adsorber	RSSCT
Bulk or bed density, $\rho_F$	g/mL	0.48	0.547
Grain Size (mesh), $d_p$	Sieve	# 8 x 30	# 200 x 400
Column diameter	cm		0.5
Column height	cm		13.5
Bed volume, BV or $V_F$			2.65 mL
Flow Rate, Q	L/min	694	0.00265
EBCT	min	20	1

In Figure 3-4, we plot the RSSCT breakthrough data.

Figure 3-4. BV Breakthrough Curve for Example Problem. Water is hypothetical with unknown characteristics other than containing 50 ug/L of perchlorate.



Note from Figure 3-4 that the treatment objective is exceeded almost immediately upon breakthrough (at about 18,400 BVs).

Specific throughput is calculated using Eqs 2-3 and 2-6

**1.) Solve for x/m (in mg/g) and Specific Throughput (in L<sub>H2O</sub>/g)**

x = amount of ClO<sub>4</sub><sup>-</sup> adsorbed = Volume of water treated x influent concentration  
(Assuming effluent concentration is negligible)

= # BVs Treated x Bed Volume x influent concentration

-

x = (# BVs)(BV)(C<sub>0</sub>) where C<sub>0</sub> is in mg/L

m = amount of GAC used to treat x = Bed Volume x GAC density

m = (BV)(ρ<sub>GAC</sub>) where ρ<sub>GAC</sub> is in g/L

C<sub>0</sub> = 50 ppb = 0.05 mg/L

ρ<sub>GAC</sub> = 0.48 g/mL = 480 g/L

$$(x/m) = \frac{(BV)(\#BV_s)(C_0)}{(BV)(\rho_{GAC})} = \frac{(\#BV_s)(C_0)}{(\rho_{GAC})} = \frac{(18,400)(0.05 \text{ mg/L})}{(480 \text{ g/L})} = 1.92 \text{ mg/g}$$

**Notice that the x/m value is independent of bed volume size. The specific throughput can now be calculated as:**

$$\text{Specific throughput} = \frac{(x/m)}{C_0} = \frac{(\#BV_s)}{(\rho_{GAC})} = \frac{(18,400)}{(480 \text{ g/L})} = 38.3 \text{ L/g}$$

**2.) Based on the above calculations, specific throughput is found to be 38.3 L water/g GAC; calculate the Annual T-GAC consumption in kg T-GAC per year based on flow rate of 10<sup>6</sup> L/d:**

**Annual GAC consumption = Flow Rate ÷ Specific Throughput**

$$\text{Annual Consumption} = \frac{(1 \times 10^6 \text{ L/d})(365 \text{ d/y})}{(38.3 \text{ L/g})(1000 \text{ g/kg})} = 9530 \text{ kg GAC per year}$$

**3.) Calculate the bed volume (BV) using equation 2-9:**

$$BV = Q * EBCT = (10^6 \text{ L/d})(1 \text{ day} / 1440 \text{ min})(20 \text{ min}) = 13,900 \text{ L} = 13.9 \text{ m}^3$$

**4.) Calculate the periodic T-GAC replacement/regeneration interval based on the flow rate of 10<sup>6</sup> L/d:**

$$\text{Interval} = \frac{V_{\text{treated}}}{Q} = \frac{(BV)(\#BV_s)}{Q} = \frac{(14000 \text{ L})(18400)}{10^6 \text{ L/d}} = 258 \text{ days} = 8.5 \text{ months}$$

**3.4 Design Assumptions**

In order to calculate the capital costs, a number of design assumptions have to be made to get an accurate result. The following design assumptions are made to mimic a real-world design.

#### **3.4.1. Number of Beds**

The T-GAC plant design is based on the flow rate and the EBCT using the “trains in parallel” system described in Chapter 2, section 2.5. The column diameter is assumed 12 feet, or a 6-foot radius, with a maximum flow rate of 2400 gpm, which translates to a maximum superficial velocity of 0.048 fps. For flow rates greater than 2400 gpm, the actual flow rate is divided by 2400 gpm and rounded up to the nearest whole number. This is the number of parallel trains in the design. Since there are two beds per train, the total number of beds is equal to twice the number of parallel trains.

#### **3.4.2 Total Volume**

The initial design parameters of number of trains and number of beds are based on flow rate and EBCT. However, each bed contains 66% T-GAC and 33% virgin GAC. The extra virgin GAC is there to contain sloughing of the tailoring agent. Thus, an additional 50% bed volume is required in the design. The minimum total bed volume is thus calculated as  $\text{Flow} \times \text{EBCT} \times 1.5$  to account for the extra virgin GAC required. The minimum bed depth is 2 feet.

The minimum total volume is then divided by the area of the column, which determines the required contactor length. This length is divided by the total number of beds, and

rounded up to the nearest foot to standardize the design. The actual total volume is then calculated using this length for each bed.

### **3.4.3 Superficial Velocity**

Superficial velocity is calculated from the flow rate entering one train divided by the area of the column. The flow rate for a single train is equal to the total flow rate divided by the number of trains in parallel. Based on the maximum flow of 2400 gpm for a 6-foot radius, the maximum superficial velocity is assumed to be 0.048 fps.

### **3.4.4 Water Properties**

All water properties (density, kinematic and dynamic viscosity) were assumed constant, taken at 60° F.

### **3.4.5 Media Properties**

#### **3.4.5.1 Sphericity, Porosity, and Density**

The sphericity and porosity of the GAC media is needed for equations 2-14 and 2-15. In personal phone conversation with Bob Parette (Parette, 2007), an environmental engineering PhD conducting post-doctorate research at PSU, commonly used values for GAC media are 40% for porosity and 0.6 for sphericity. These values are assumed for this model.

The GAC used in the PSU tests had a density of 480 g/L for an 8 x 30 mesh grain size, and a density of 540 g/L for the 200 x 400 mesh grain size used in the RSSCT experiments, which translates into 29.9 and 33.6 PCF respectively. For purposes of this

cost model, the grain sizes for 12 x 40, 20 x 40, and 20 x 50 mesh is estimated to be 30.1, 31.0, and 31.1 PCF respectively.

#### **3.4.5.2 Grain Size**

The average particle diameter was calculated using the geometric mean. Final results were as follows:

Table 3-3. Average particle diameters for various mesh sizes

GAC Media Mesh Size	Average Particle Diameter in mm, $d_p$
200 x 400	.059
20 x 50	.499
20 x 40	.594
12 x 40	.840
8 x 30	1.19

#### **3.4.6 EBCT Scaling**

The EBCT was scaled based upon equation 2-12, assuming proportional diffusivity (and thus,  $X = 1$ ). The percent achieved true equilibrium was based on Figure 3-3. Particle diameters are shown in Table 3-3. The final results are as follows in Table 3-4:

Table 3-4. Effect of grain size on EBCT in scaling

<b><u>200 x 400</u></b> EBCT	<b><u>20 x 50</u></b> EBCT	<b><u>20 x 40</u></b> EBCT	<b><u>12 x 40</u></b> EBCT	<b><u>8 x 30</u></b> EBCT	Percent Achieved True Equilibrium
(minutes)	(minutes)	(minutes)	(minutes)	(minutes)	
0.25	2.10	2.5	3.54	5	35%
0.35	2.94	3.5	4.95	7	66%
0.4	3.36	4.0	5.66	8	76%
0.5	4.20	5.0	7.07	10	88%
0.6	5.04	6.0	8.49	12	90%
0.75	6.30	7.5	10.61	15	92%
1	8.40	10	14.15	20	95%
2	16.8	20	28.30	40	96%

Example: Convert the RSSCT 200 x 400 mesh EBCT of 1 minute to the EBCT for an 8 x 30 mesh using equation 2-12. Assume proportion diffusivity ( $X = 1$ ).

Per equation 2-12:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[ \frac{d_{p,SC}}{d_{p,LC}} \right]^{2-X} \quad (2-12)$$

Given:  $EBCT_{SC}$  = RSSCT EBCT (200 x 400) = 1 minute  
 $d_{p,SC}$  = RSSCT particle diameter = 0.059 (from Table 3-5)  
 $d_{p,LC}$  = 8 x 30 particle diameter = 1.19 (from Table 3-5)

Solution: Solve for  $EBCT_{LC}$  using equation 2-12 ( $X = 1$ ).

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \frac{1 \text{ min}}{x \text{ min}} = \left[ \frac{0.059}{1.19} \right]$$

$$x = \frac{(1 \text{ min})(1.19)}{0.059} = 20 \text{ min}$$

Therefore, the results for an RSSCT run at an EBCT of 1 minute are predicted to be the same results as for an 8 x 30 mesh run at an EBCT of 20 minutes.

### **3.4.7 Predicted # BVs to breakthrough**

The predicted # BVs to breakthrough is based on equation 3-4, with the competition coefficients determined as noted above in section 3.2.3. The model uses simulated EBCTs for the 8 x 30 mesh size, scaled up from RSSCT results by PSU using equation 2-12 as demonstrated above. The EBCTs for the other meshes that relate to the EBCT for the 8 x 30 mesh are found using equation 2-12.

### **3.5 Cost Calculations**

The cost calculations are based on both the cost assumptions in Table 3-5 and the design assumptions in section 3.4.

#### **3.5.1 Cost Assumptions**

Cost analyses will determine the annualized cost of the system, considering capital costs, media costs, labor costs, and disposal costs. The cost assumptions are annotated in Table 3-5.

Table 3-5. Cost assumptions

Cost Category	Unit Cost	Units	Notes
Initial capital costs	\$12.00	lb of GAC	Rough estimate including startup costs, testing, mobilization, contactors, GAC media, site-specific design and construction requirements, labor, and ancillary equipment (tools, piping, etc.)
GAC media costs	\$1.50	lb of GAC	Cost for media replacement
GAC change-out labor and transport	\$5,000	Per bed	Labor for media replacement
Disposal by incineration	\$10.00	per CF of GAC	Cost for disposal of media
Discount rate		%	User input, to annualize capital costs
Useful life		Years	User input, to annualize capital costs
Power costs		per kW-hr	User input, cost for power to pump water through media. Assumed continuous operation
Pump efficiency	70%		Used to estimate the efficiency of the pump in calculating power requirements
Thermal Regeneration?		Yes or No	User input 1 = yes, 0 = no

### **3.5.2 Initial Capital Costs**

Initial capital costs are those costs associated with installing a complete filtration system, including, but not limited to, startup costs, testing, mobilization, filter vessels, GAC media, site-specific design and construction/site preparation, labor, and ancillary equipment (tools, piping, etc.). Chapter 2 cited a study conducted in 1998 that found that initial capital costs can be estimated as approximately \$8 per lb GAC. Using the Chemical Engineering Plant Cost Index (CE PCI, 2006), the unit capital costs are conservatively estimated at \$12 per lb GAC. Calculations are as follows:

$$\begin{aligned} 1998 \text{ CE PCI} &= 389.5 \\ 2006 \text{ CE PCI} &= 486.6 \end{aligned}$$



Cost = \$8 per lb \* (486.6/389.5) = \$10 per lb GAC: Used \$12 per lb to be conservative

Costs were based on the density of GAC and the actual total bed volume as discussed in section 3.4.1. Converting the design into a present worth capital cost is demonstrated in Appendix E. The initial capital cost is converted to an annuity using the discount rate using equation 2-17 as we recall from Chapter 2 by:

$$A = PW * \frac{i(1+i)^n}{(1+i)^n - 1} \quad (2-17)$$

Where:      i = discount rate [%]  
              A = Annuity or Annual Worth [\$]  
              PW = Present Worth [\$]  
              n = expected useful life [years]

The discount rate and expected useful life is input by the user.

### **3.5.3 Operating and Maintenance Costs**

#### **3.5.3.1 Calculating the number of change-outs, or services, per year**

A change-out expense is assumed to have occurred when both beds of GAC have been completely exhausted. While this is not completely true, as change-outs actually occur when the lead vessel is exhausted, considering both beds as a change-out period yields the same result and simplifies the calculation.

The volume of water treated by one bed volume is simply the predicted # BVs treated to break through (from equation 3-4 and Table 3-4) times the actual total bed volume.

The number of days between change-outs is calculated simply as the volume of water treated divided by the actual flow rate, converted to days.

The number of change-outs per year is then calculated simply as 365 days per year divided by the number of days between change-outs.

### **3.5.3.2 GAC Replacement Costs**

Chapter 2 cited a vendor quote from USFilter giving cost range for coal-based GAC media from \$0.80 to \$1.50 per pound, and a service charge for labor of \$5,000 per bed. To be conservative, both the T-GAC and virgin GAC are estimated at \$1.50 per pound. Change-out labor is estimated as the vendor quote of \$5,000 per bed. For purposes of this model, the operating and maintenance costs aren't expected to increase from year to year.

The amount of GAC used per year is simply calculated as the number of change-outs times the actual bed volume. This is multiplied by \$1.50 per lb cost of GAC to get the annual GAC media costs.

The annual change-out labor is calculated as \$5,000 times the number of change-outs per year times the total number of beds.

### **3.5.3.3 GAC Disposal Costs**

Chapter 2 cited a study conducted by the Federal Remediation Technologies Roundtable (FRTR, 2007), which found that unit costs associated with ex situ incineration of

hazardous waste-contaminated soil ranged from \$40 to \$44 per cubic foot. However, it is not assumed that the cost for incinerating contaminated spent GAC will be similar to that of incinerating contaminated soil. According to Dr. Cannon's experience with thermal disposal costs of GAC, the unit costs are closer to \$10 per cubic foot (Cannon, 2007). For this model, unit disposal costs are assumed to be \$10 per cubic foot.

Disposal costs are based upon the amount of GAC used per year, as noted in section 3.4.4.2. For purposes of this model, the disposal costs aren't expected to increase from year to year.

#### **3.5.3.4 Power Costs**

Headloss and power requirements are calculated in accordance with equations 2-15 and 2-16, with a total length and actual superficial velocity as calculated in section 3.4.1. However, the pump required to overcome the calculated headloss is not 100% efficient. To account for power losses in the pump, the pump is conservatively assumed to be only 70% efficient.

Power rates vary from place to place, and are usually give as a unit rate in kilowatt-hours (kW-hr). Therefore, power unit cost is a user input. According to equation 2-15, power is calculated in Watts, which is easily converted to kilowatts. Assuming continuous operation, to get an annual cost, the total power requirement is multiplied by the number of hours per year by the unit power cost per kW-hr. For purposes of this model, the annual power costs aren't expected to increase from year to year.

### **3.5.3.5 Potential Impact of Thermal Regeneration**

Thermal regeneration of exhausted GAC can produce cost benefits in two ways. First, it can potentially reduce the cost of purchasing new GAC media, as noted in section 2.5.2. Savings potential ranges from \$0.20 to \$0.40 per lb. Typical savings are approximately \$0.30 per lb (Cannon, 2007). For purposes of this model, the media unit cost savings due to thermal regeneration are assumed at \$0.30 per lb.

Second, GAC that is regenerated does not need to be disposed of, thus eliminating disposal costs. Therefore, unit disposal costs are estimated at \$0 when assuming thermal regeneration.

A negative factor that must be considered is that GAC that has been regenerated has less loading capacity than new GAC. The loading capacity of regenerated GAC is typically only 85% of new GAC (Cannon, 2007). Additionally, 5% of the GAC media is lost during the thermal regeneration process. Therefore, these factors are included in the model when assuming the use of thermal regeneration. The final assumptions for costs associated with thermal regeneration are noted in Table 3-6.

Table 3-6: Assumptions for Thermal Regeneration of GAC

Media Savings	\$0.30	per lb GAC
Disposal Costs	\$0	per lb GAC
Capacity Lost	15%	
Media Lost	5%	

#### **3.5.4 Cost Sensitivity Analysis**

The sensitivity of cost to discount rate, economic life, EBCT, and potential cost savings if T-GAC is replaced or regenerated will be explored.

## **IV. Results and Discussion**

### **4.1 Introduction**

The purpose of this chapter is to develop the design-cost screening model and apply it to determine how predictions of cost and performance of T-GAC systems are affected by assumptions regarding model parameter values, unit costs, and influent water quality. An outline of the chapter follows:

1. Determination of Parameter Values
2. Final Design-Cost Screening Tool (Appendix E)
3. Model Predictions of T-GAC Performance
  - a. Examination of Parameter K
  - b. Examination of Parameter 1/n
  - c. Sensitivity of results to competing ion coefficients
  - d. Sensitivity of results to influent water quality
4. Model Predictions of Cost

### **4.2 Determination of Parameter Values**

Section 3.2 explains the methodology used to determine the parameter values in the performance model.

#### **4.2.1 Determination of Freundlich Parameter K**

The Freundlich parameter K was determined using equations 3-1 to 3-3 for distilled-deionized water spiked with 1 mg/L perchlorate and run through an RSSCT with an EBCT of 20 minutes simulated for an 8 x 30 mesh. For this run, the GAC density was 480 g/L, the # BVs treated was 14250, and Table 3-4 was used to estimate the percent achieved true equilibrium at 95%. This resulted in the following calculations:

$$(x/m)_{ClO_4} = \frac{(\#BVsTreated)(C_{0,ClO_4})[mg/L]}{\rho_F[g/L]} = \frac{(14250)(1mg/L)}{(480g/L)} = 29.7mg/g$$

$$K_{ClO_4} = (x/m)_{ClO_4} / (95\% * (1 \text{ mg} / \text{L})^{1/n}) = 29.7 / 0.95 = 31.3 (\text{mg} / \text{g})(\text{L} / \text{mg})^{1/n}$$

Therefore, K was initially estimated at  $31.3 (\text{mg/g})(\text{L/mg})^{1/n}$ .

#### **4.2.2 Determination of Freundlich Parameter 1/n**

The value for 1/n was found by keeping K constant at  $31.3 (\text{mg/g})(\text{L/mg})^{1/n}$ , allowing the Solver program to vary the value for 1/n along with the competition coefficients, and running an optimization to minimize total error. The value for 1/n that resulted in the lowest total error after optimization was 0.156. This Solver-optimized solution produced a total error of 47.0%, with a mean error of 4.28% and a standard deviation of 6.94% over the 11 different water chemistries analyzed.

#### **4.2.3 Determination of Competition Coefficients**

The values for the competition coefficients were found by keeping K and 1/n constant at the above values, and running a Solver optimization that varied the competition coefficients until a solution was found that minimized the total error. All ions without associated data were not included in the optimization runs. Sulfate's competition coefficient was estimated as 0.0 (no effect) based on PSU RSSCT data that showed no change in performance associated with significant changes in Sulfate concentrations. The initial optimized values for the optimized competition coefficients explored in this research are listed in Table 4-1.

Table 4-1: Initial Optimized Competition Coefficient Values

Ion (Concentrations in mg/L)	Competition Coefficient, $a_j$
Nitrate ( $\text{NO}_3^-$ )	0.0178
Thiosulfate	0.351
Sulfate ( $\text{SO}_4^{2-}$ )	0
Chloride	0
Bicarbonate	0.000208

#### **4.2.4 Final Determination of all Parameters**

The Solver model was allowed to change all values simultaneously, including  $K$ ,  $1/n$ , and the competition coefficients, to obtain the lowest possible total error. Final optimized values for all parameters are listed in Table 4-2.

Table 4-2: Final Optimized Parameters for Freundlich Multi-component Isotherm

Ion (Concentrations in mg/L)	Competition Coefficient, $a_j$
Nitrate ( $\text{NO}_3^-$ )	0.0169
Thiosulfate	0.332
Sulfate ( $\text{SO}_4^{2-}$ )	0
Chloride	0
Bicarbonate	0.000226
$K = 30.3 \text{ (mg/g)(L/mg)}^{1/n}$	$1/n = 0.153$

These are the values used in the final cost model. This Solver-optimized solution produced a total error of 43.8%, with a mean error of 3.99% and a standard deviation of 6.41%, a slight improvement from the previous optimization, where optimal values for  $K$ ,  $1/n$ , and the competition coefficients were obtained separately.

### **4.3 Final Design-Cost Screening Tool**

A full explanation of the final design-cost model is located in Appendix E.



#### **4.4 Model Predictions of T-GAC Performance**

Results: The ability of the calibrated model to closely simulate RSSCT results varies, and is highly dependent on the model parameters. A total of 6 parameters were varied by Solver – K,  $1/n$ , and the competition coefficients for nitrate, chloride, thiosulfate, and bicarbonate. Obviously, the more parameters that can be varied when calibrating the model, the better the fit obtained. One goal is to achieve the best fit while minimizing the number of fitting parameters; in this regard, if a model parameter is identified that doesn't affect simulated results, it can be eliminated.

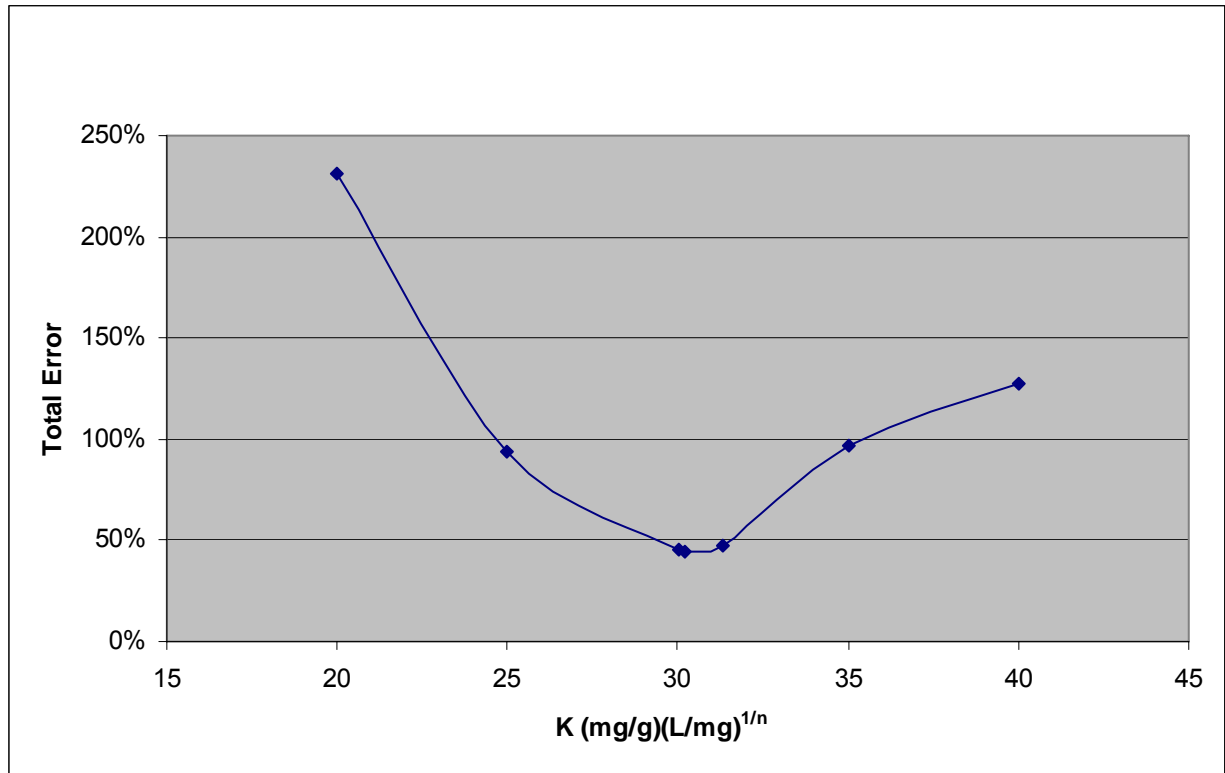
Using the value of K as  $31.3 \text{ (mg/g)(L/mg)}^{1/n}$ , which was obtained from the de-ionized water RSSCT run containing 1 mg/L perchlorate and 20 minute EBCT, and an assumed  $1/n$  value of 0.42 that is within the range obtained by others (Chen et al., 2005a), the model was calibrated by varying the competition coefficients. This resulted in a total error of 158%, with a mean error for each RSSCT experiment of 14.4% and a standard deviation of 20.2%. However, when the model used both K and  $1/n$ , as well as the competition coefficients for calibration, the total error was 43.8%, with a mean error of 3.99% and a standard deviation of 6.41%. The K and  $1/n$  values associated with this optimization were  $30.3 \text{ (mg/g)(L/mg)}^{1/n}$  and 0.153 respectively.

##### **4.4.1 Examination of parameter K**

The sensitivity of model results to changes in the Freundlich parameter K was examined by changing the values of K from 20 to 35  $\text{(mg/g)(L/mg)}^{1/n}$  and having the model

optimize the competition coefficients for each K (while holding  $1/n$  constant). The results were graphed, as shown in Figure 4-1.

Figure 4-1: Plot of Freundlich K vs. Total Error ( $1/n = 0.15$ )



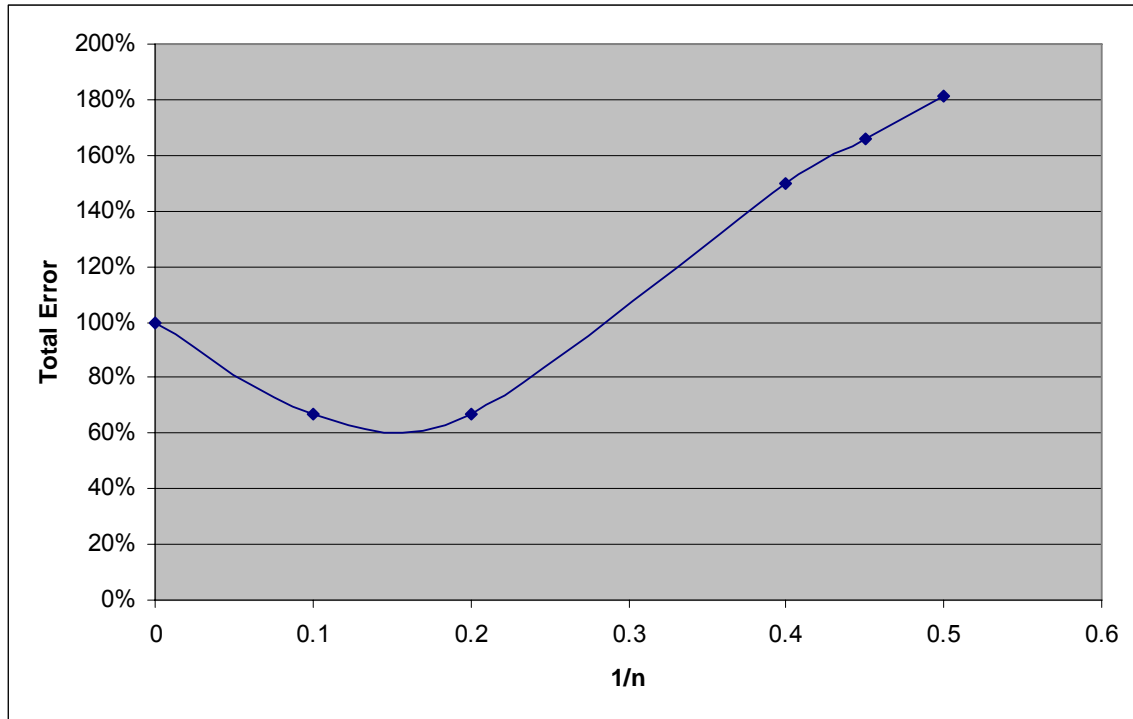
From Figure 4-1, it appears that the value of K that produces the best fit of the model simulations to RSSCT results is between 30 and 32 (mg/g)(L/mg)<sup>1/n</sup>. This is consistent with section 4.2.4, where a best-fit value of K of 30.3 (mg/g)(L/mg)<sup>1/n</sup> was obtained, when the model calibrated all parameters simultaneously. Similar results were obtained for varying values of  $1/n$ , and thus it appears the best-fit value of K is independent of  $1/n$ .

#### **4.4.2 Examination of parameter $1/n$**

The sensitivity of model results to changes in the Freundlich parameter  $1/n$  was examined by changing the value of  $1/n$  from 0.4 to 0.5 and having the model optimize the

competition coefficients for each  $1/n$  (while holding  $K$  constant). The results were graphed, as shown in Figure 4-2.

Figure 4-2: Plot of Freundlich  $1/n$  vs. Total Error ( $K = 31.3 \text{ (mg/g)(L/mg)}^{1/n}$ )



From Figure 4-2, it appears the best-fit value of  $1/n$  is about 0.15, which is consistent with section 4.2.4, where a best-fit value of  $1/n$  of 0.153 was obtained, when the model calibrated all parameters simultaneously. Similar results were obtained for varying values of  $K$ . It is somewhat surprising that the value of  $1/n$  found here is so different than the values of  $1/n$  reported in the literature (0.4 – 0.5). Therefore, it is hypothesized that the adsorption behavior for perchlorate adsorption onto T-GAC using the surfactants in this research is different from the literature values for other surfactants. Another potential explanation for the unexpected value of  $1/n$  is due to an assumption of the Freundlich multi-component isotherm. That assumption is that the parameter values,  $K$

and  $1/n$ , are independent of competing ion concentrations. The unexpectedly low value of  $1/n$  may result from this assumption not applying to perchlorate adsorption on T-GAC.

#### **4.4.3 Sensitivity of results to competing ion competition coefficient**

The competition coefficients,  $a_j$ , were optimized by the model to minimize total percent error. The potential competing ions that were studied include nitrate, thiosulfate, chloride, and bicarbonate. Based on numerous optimizations, varying both  $K$  and  $1/n$ , the following observations were made about each potential competing ion:

Sulfate: As discussed in Appendix F, PSU RSSCTs showed that sulfate did not to compete for T-GAC adsorption sites, so sulfate was not considered as a competing ion.

Chloride: The value of the competition coefficient for chloride was optimized at very close to zero in all model optimization runs. Therefore, it is assumed that chloride does not compete with perchlorate for adsorption sites on the T-GAC, and it was eliminated from the model.

Nitrate: The optimized value of the competition coefficient for nitrate was between 0.01 and 0.02, for varying values of  $K$  and  $1/n$ . By manually varying the competition coefficient for nitrate for  $1/n = 0.153$ , it was found that a value of 0.017 for the nitrate competition coefficient minimized the total percent error. Using the literature values of  $1/n$  of 0.4 to 0.5, the optimized nitrate competition coefficient value ranges from 0.014 to

0.016. Thus, it appears the competition coefficient for nitrate for use in the model is somewhere between 0.014 and 0.017.

Nitrate discussion: The nitrate competition coefficient calibration exercise produced fairly consistent results. PSU RSSCT experiments with varying concentrations of nitrate in Fontana water show that nitrate does indeed impact performance. While the competition coefficient may be relatively small, the significant concentrations of nitrate found in the Fontana and Redlands waters (16 to 34 ppm) in comparison to perchlorate (7 to 75 ppb) translates into significant competition and an impact on system performance.

Thiosulfate: Calibration of the thiosulfate competition coefficient resulted in values between 0.3 and 1.0 for varying values of  $K$  and  $1/n$ . By manually varying the competition coefficient for thiosulfate for  $1/n = 0.153$ , it was found that a value of 0.3 for the thiosulfate competition coefficient minimized the total percent error. Using the literature values of  $1/n$  of 0.4 to 0.5, the optimized thiosulfate competition coefficient value ranges from 0.7 to 1.0. Thus, it appears the competition coefficient for thiosulfate is somewhere between 0.3 and 1.0.

Thiosulfate discussion: The thiosulfate competition coefficient calibration exercise produced a relatively large range of values; with the value significantly dependent on the assumed value of  $1/n$ . PSU RSSCT experiments with distilled-deionized water containing 1 mg/L perchlorate with varying concentrations of thiosulfate show that thiosulfate has a significant impact on performance (see RSSCT runs 6 – 10 in Appendix

F). The relative magnitude of the competition coefficient values (0.3 – 1.0) confirm that thiosulfate is a strong competitor for adsorption sites.

Bicarbonate: The optimized value of the competition coefficient for bicarbonate was between 0.0 and 0.001, for varying values of K and  $1/n$ . By manually varying the competition coefficient for bicarbonate for  $1/n = 0.153$ , it was found that a value of 0.00022 for the bicarbonate competition coefficient minimized the total percent error. Using the literature values of  $1/n$  of 0.4 to 0.5, the optimized bicarbonate competition coefficient value ranges from 0 to 0.001. Thus, it appears the competition coefficient for bicarbonate for use in the model is somewhere between 0.00022 and 0.001.

Bicarbonate discussion: The bicarbonate competition coefficient calibration exercise produced a relatively large range of values; with the value significantly dependent on the assumed value of  $1/n$ . As with nitrate, bicarbonate can have a significant impact on performance due to its presence in relatively large concentrations with respect to perchlorate.

General discussion: Of the suspected competing ions examined, the nitrate competition coefficient had a narrow range, with values that were relatively independent of the assumed value of  $1/n$ . The competition coefficient for thiosulfate was relatively large, and much more dependent on the assumed  $1/n$  value. The competition coefficient for bicarbonate was small, with values dependent on the assumed value of  $1/n$ . Because of the very low magnitude of the bicarbonate competition coefficient, it is unclear if

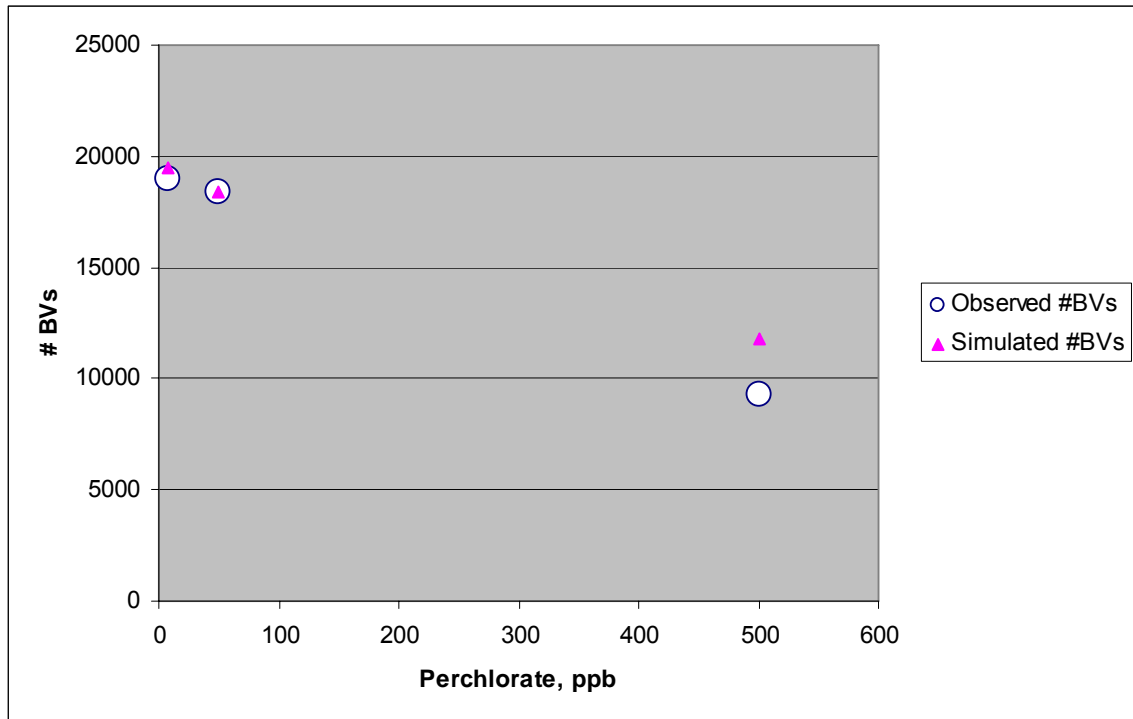
bicarbonate is competing with perchlorate for adsorption sites or if the competition coefficient is an experimental artifact.

#### **4.4.4 Sensitivity of results to influent water quality**

There were four different waters used in developing this model: Fontana well #17C, Distilled-Deionized, Redlands, and Massachusetts. Each is examined and discussed below.

Four RSSCTs used Fontana well #17C water: 1.) Unamended Fontana water containing approximately 7 ppb perchlorate; 2.) Fontana water spiked to 50 ppb perchlorate; 3.) Fontana water spiked to 500 ppb perchlorate; and 4.) Fontana water spiked to 100 ppm nitrate. Results from two additional RSSCTs using sulfate-spiked Fontana water were used to determine that sulfate did not compete with perchlorate for adsorption sites. A comparison between #BVs experimentally observed in the RSSCTs and model-predicted #BVs can be seen in Figure 4-3. The salient characteristics of the #BVs vs perchlorate concentration relation were reproduced by the model regardless of the value of  $1/n$  that was assumed.

Figure 4-3: Comparison of #BVs Observed in RSSCT vs. Simulated #BVs for Fontana Water Spiked with Perchlorate ( $K = 30.3 \text{ (mg/g)(L/mg)}^{1/n}$ ,  $1/n = 0.153$ )



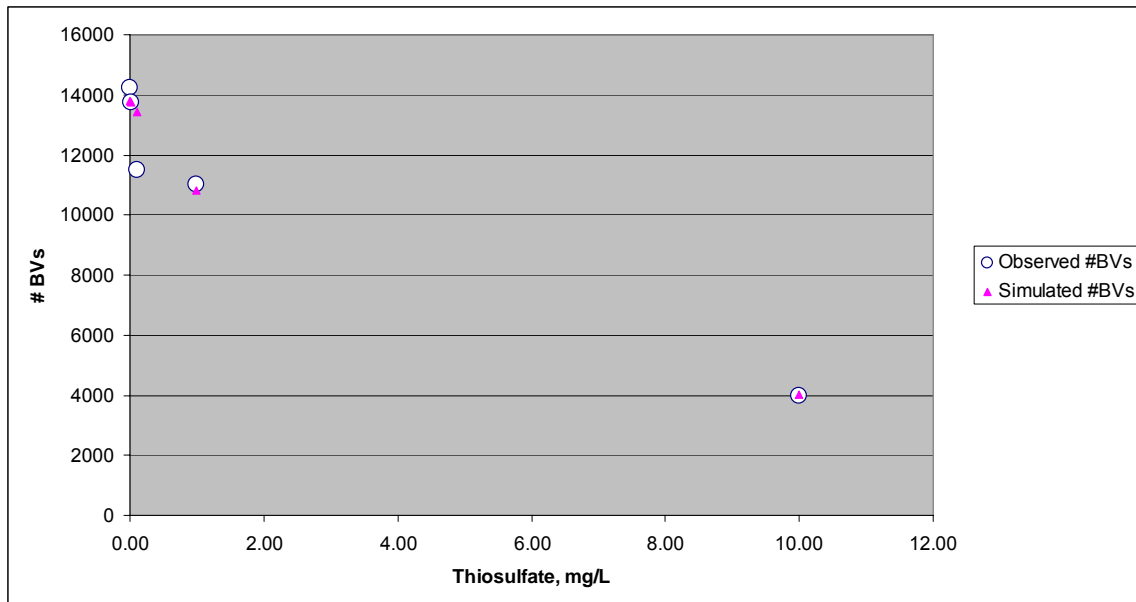
Fontana water discussion: Although based on only three RSSCTs, there appears to be a linearly inverse relation between perchlorate concentration and #BVs for Fontana water spiked with perchlorate. The model also simulates a linearly inverse relationship.

Five RSSCTs used distilled-deionized water, all spiked with 1 ppm perchlorate and varying concentrations of thiosulfate: 1.) Distilled-deionized water containing only 1 ppm perchlorate; 2.) Distilled-deionized water with 1 ppm perchlorate and also spiked with 0.01 ppm thiosulfate; 3.) Distilled-deionized water with 1 ppm perchlorate and also spiked with 0.1 ppm thiosulfate; 4.) Distilled-deionized water with 1 ppm perchlorate and also spiked with 1 ppm thiosulfate; and 5.) Distilled-deionized water with 1 ppm perchlorate and also spiked with 10 ppm thiosulfate. A comparison between #BVs



experimentally observed in the RSSCTs and model-predicted #BVs can be seen in Figure 4-4. The salient characteristics of the #BVs vs thiosulfate concentration relation were reproduced by the model regardless of the value of  $1/n$  that was assumed.

Figure 4-4: Comparison of #BVs Observed in RSSCT vs. Simulated #BVs for Distilled Water Spiked with 1 ppm Perchlorate and Varying Concentrations of Thiosulfate ( $K = 30.3 \text{ (mg/g)(L/mg)}^{1/n}$ ,  $1/n = 0.153$ )



Distilled-deionized water discussion: By keeping the perchlorate concentration constant, the effect of thiosulfate can be analyzed. The model was able to simulate the increase in #BVs experimentally observed as thiosulfate concentrations approach 0.0, although the magnitude of the increase at a thiosulfate concentration of 0.1 ppm was overestimated by the model.

Only one RSSCT run (RSSCT run 10) with Redlands water was used to determine model parameters (see Appendix C). As discussed in Section 3.3.1, the other RSSCT runs with Redlands water were used to develop the EBCT relationship curve (Figure 3-2).

Redlands water discussion: Using the final parameter values in Table 4-2, the model calculated the #BVs to breakthrough at approximately 32,000 compared to 34,000 obtained from the RSSCT results, a difference of 6.3%. The model was optimized for several values of  $1/n$ , as shown in Figure 4-2. As  $1/n$  approached zero, the error for the model calculation of #BVs for Redlands water approached zero although total error for all 11 runs increased, as shown by Figure 4-2. This error remains relatively low ( $< 40\%$ ) as the value for  $1/n$  approaches 0.5.

Only one RSSCT run (RSSCT run 11) with Massachusetts (MA) water was used to determine model parameters (see Appendix C). Using the final parameter values in Table 4-2, the model calculated the #BVs to breakthrough at approximately 210,300 compared to 210,000 obtained from the RSSCT results, a negligible difference of 0.14%. This error becomes high ( $> 40\%$ ) as  $1/n$  approaches zero, and very high ( $>> 50\%$ ) as  $1/n$  approaches 0.5. The ability of the model to accurately simulate the RSSCT results for Massachusetts water appears highly sensitive to the value of  $1/n$ .

#### **4.5 Model Predictions of Cost**

Costs for treating each of the waters in Appendix C were estimated using the assumptions in Chapter 3, and user-input assumptions of 15 year useful life, 3% discount rate, and

\$0.10 per kW-hr cost for power for a flow rate of 5000 gpm. Costs for two additional waters (Fontana well 22 water at two different perchlorate concentrations) were also estimated. The results are shown in Table 4-3.

Table 4-3: Model Cost Predictions for Waters Analyzed in RSSCT Runs 1 through 11 (Appendix C) and Fontana Well 22 Water with Added Perchlorate.

RSSCT Run #	Water	ClO <sub>4</sub> - Ppb	High \$/acre-ft	Low \$/acre-ft
1	Fontana Well 17C	7	\$560	\$217
2	Fontana Well 17C	50	\$593	\$227
3	Fontana Well 17C	500	\$919	\$334
4	Fontana Well 17C, spiked 100 ppm nitrate	7	\$1,349	\$472
5	Distilled Deionized	1000	\$848	\$311
6	Distilled Deionized, spiked 10 ppb thiosulfate	1000	\$850	\$311
7	Distilled Deionized, spiked 100 ppb thiosulfate	1000	\$872	\$318
8	Distilled Deionized, spiked 1 ppm thiosulfate	1000	\$1,078	\$385
9	Distilled Deionized, spiked 10 ppm thiosulfate	1000	\$2,901	\$963
10	Redlands	75	\$379	\$154
11	Massachusetts	5.6	\$93	\$23
	Fontana Well 22	400	\$613	\$234
	Fontana Well 22	1000	\$1,041	\$373
	* Note the water chemistry for Fontana Well 22 contains 14 ppm NO <sub>3</sub> <sup>-</sup> , 32 ppm SO <sub>4</sub> <sup>2-</sup> , 18 ppm Cl <sup>-</sup> , and 180 ppm bicarbonate			

Note that costs to treat the Massachusetts water, which has low levels of perchlorate and competing ions, are attractively low.

Also note the relatively large difference between the high and low cost estimates. The high estimate is generally up to three times the low estimate. As will be described in more detail below, the high estimates result from treating water with high concentrations

of perchlorate and competing ions using a low EBCT. The low EBCT leads to the assumption that treatment is far from equilibrium (see Table 3-4). The savings in initial capital costs that are achieved by having a low EBCT are far outweighed by the additional costs for GAC replacement and disposal that are required at a low EBCT. However, when there are low concentrations of perchlorate and competing ions, such as for the Massachusetts water, the high estimates are for the higher EBCTs, where the additional capital costs needed for the high EBCT outweigh the relatively small savings in replacement and disposal costs that are gained at these low concentrations. A detailed analysis of the cost estimation results follows.

#### **4.5.1 Cost Breakdown**

Tables 4-4 to 4-7 show the percentage of total cost associated with power, capital, and GAC replacement (including change-out labor) for various waters and various EBCTs.

Table 4-4: Cost Breakdown for Redlands Water at Various EBCTs

Simulated 20 x 40 mesh				
EBCT minutes	% Power Costs	% Capital Costs	% GAC Replacement	Total
2.5	0.27%	2.77%	96.96%	100%
3.5	0.77%	7.81%	91.42%	100%
4.0	0.88%	8.88%	90.24%	100%
5.0	1.32%	13.35%	85.33%	100%
6.0	1.49%	15.15%	83.35%	100%
7.5	1.95%	19.79%	78.26%	100%
10.0	2.39%	24.24%	73.37%	100%
20.0	3.92%	39.77%	56.31%	100%

Table 4-5: Cost Breakdown for Fontana Well 17C Water at Various EBCTs

Simulated 20 x 40 mesh				
EBCT minutes	% Power Costs	% Capital Costs	% GAC Replacemen t	Total
2.5	0.18%	1.87%	97.94%	100%
3.5	0.53%	5.38%	94.09%	100%
4.0	0.61%	6.14%	93.25%	100%
5.0	0.93%	9.39%	89.68%	100%
6.0	1.06%	10.74%	88.21%	100%
7.5	1.41%	14.27%	84.32%	100%
10.0	1.75%	17.80%	80.45%	100%
20.0	3.07%	31.11%	65.82%	100%

Table 4-6: Cost Breakdown for Massachusetts Water at Various EBCTs

Simulated 20 x 40 mesh				
EBCT minutes	% Power Costs	% Capital Costs	% GAC Replacemen t	Total
2.5	3.25%	33.01%	63.74%	100%
3.5	5.65%	57.34%	37.01%	100%
4.0	5.94%	60.28%	33.78%	100%
5.0	6.79%	68.91%	24.30%	100%
6.0	7.03%	71.33%	21.64%	100%
7.5	7.49%	75.95%	16.57%	100%
10.0	7.79%	79.02%	13.19%	100%
20.0	8.38%	84.98%	6.64%	100%

Table 4-7: Cost Breakdown for Distilled De-ionized Water Spiked with 1 mg/L Perchlorate at Various EBCTs

Simulated 20 x 40 mesh				
EBCT minutes	% Power Costs	% Capital Costs	% GAC Replacemen t	Total
2.5	0.12%	1.24%	98.64%	100%
3.5	0.36%	3.60%	96.04%	100%
4.0	0.41%	4.12%	95.47%	100%
5.0	0.63%	6.38%	92.99%	100%
6.0	0.72%	7.34%	91.94%	100%
7.5	0.98%	9.89%	89.13%	100%
10.0	1.23%	12.51%	86.26%	100%

20.0	2.28%	23.12%	74.60%	100%
------	-------	--------	--------	------

When performing these calculations for different mesh sizes (8 x 30, 12 x 40, 20 x 50), the cost breakdown results are similar (results are not shown).

Notice that for Fontana and Redlands waters, the GAC disposal and replacement costs typically dominate, even at high EBCTs. This is due to the high concentrations of competing ions in the water, particularly nitrate. Due to these high concentrations, the GAC is rapidly exhausted, so GAC replacement costs dominate total costs.

For the distilled de-ionized water spiked with a high concentration of perchlorate (1 mg/L), the GAC disposal and replacement costs once again dominate. This is expected as the high concentrations of perchlorate exhaust the GAC more rapidly than low concentrations.

For Massachusetts water, the capital costs typically dominate. Without competing ions, and with only low concentrations of perchlorate present, GAC replacement is infrequent, so replacement costs are low.

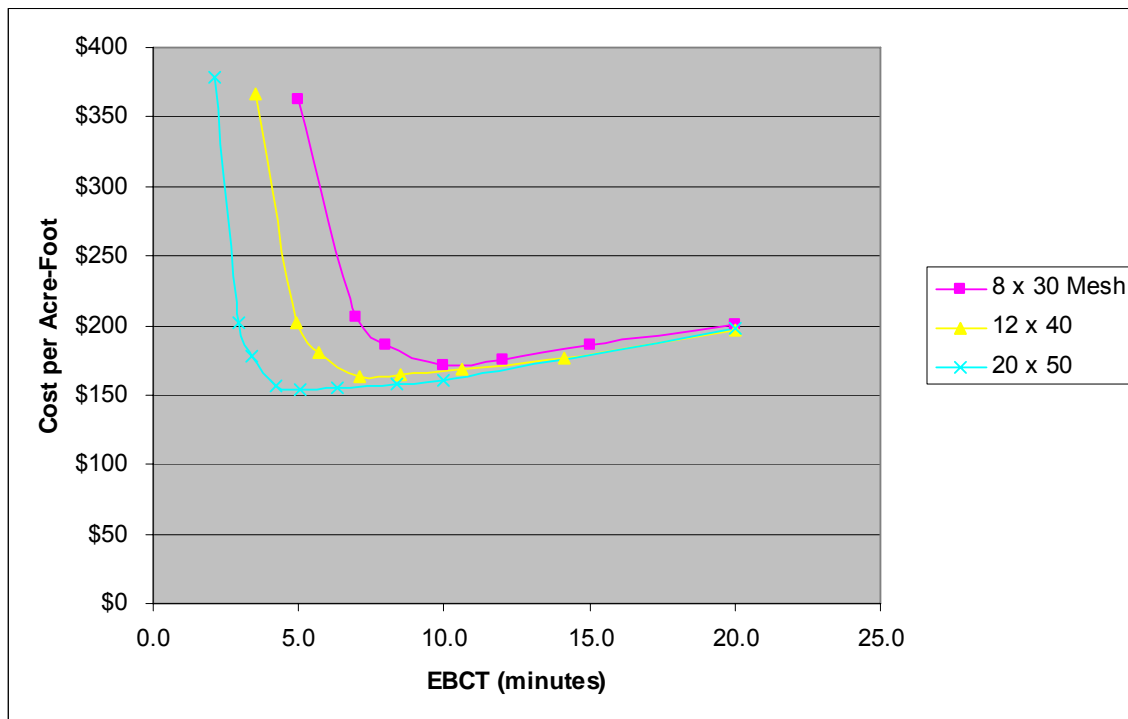
#### **4.5.2 Cost Sensitivity Analysis – EBCT and Water Chemistry**

Analyses of the sensitivity of costs to EBCT and concentrations of perchlorate, nitrate, thiosulfate, and bicarbonate were conducted. Except as noted, the sensitivity analyses were for Redlands water, using the cost assumptions noted previously (15 year useful life, 3% discount rate, and \$0.10 per kW-hr).

#### **4.5.2.1 Sensitivity to EBCT**

Tables 4-4 to 4-7 showed how EBCT affected the relative breakdown of costs as a function of EBCT. Here, Figure 4-5 shows how total cost per acre-foot of water treated changes with EBCT.

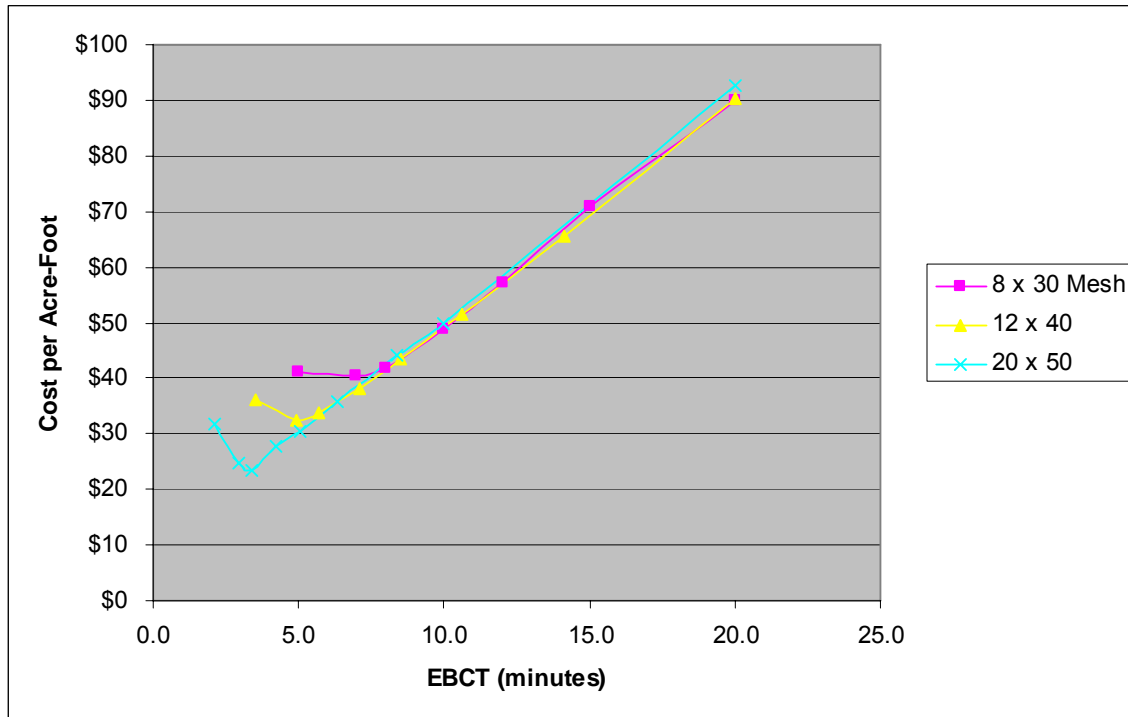
Figure 4-5: Cost per Acre-Foot as a Function of EBCT for Redlands Water.



From Figure 4-5 one can discern how there is an optimal EBCT and mesh size that minimizes treatment costs for Redlands water. In this case, a 5 minute EBCT and 20 x 50 mesh size results in the lowest cost. Note that cost is extremely sensitive to EBCT when EBCTs are low. This is because at low EBCTs, it is assumed that the adsorbed concentrations are very far from equilibrium with the dissolved concentrations, so breakthrough is relatively rapid (see Table 3-4) and GAC replacement costs are high.

The impact of EBCT was analyzed for Massachusetts water as well (Figure 4-6).

Figure 4-6: Cost per Acre-Foot as a Function of EBCT for Massachusetts Water



From Figure 4-6 we observe that the unit treatment costs are much more sensitive to EBCT for Massachusetts water than for Redlands water. This is because the total costs for Massachusetts water, which has low concentrations of perchlorate and competing ions, are dominated by capital costs, and the main determinant of the capital cost is the EBCT (see Table 4-6).

#### **4.5.2.2 Sensitivity to Perchlorate Concentrations**

As expected, the cost per acre-foot of water treated increases with increases in perchlorate concentrations. For distilled de-ionized water, the impact of perchlorate alone can be analyzed, as shown in Figure 4-7.



Figure 4-7: Cost per Acre-Foot as a Function of Perchlorate Concentration in Distilled De-ionized Water.

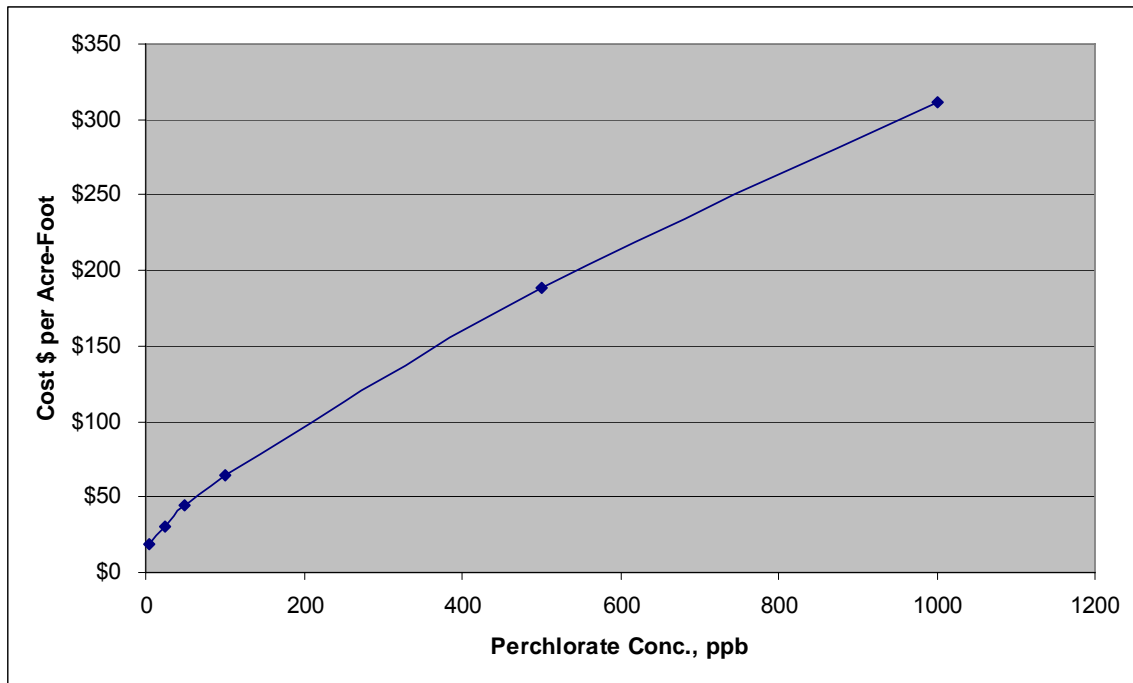


Figure 4-7 shows cost is highly sensitive to perchlorate concentration. At a perchlorate concentration of 25 ppb, the predicted cost is \$31 per acre-foot, while the cost to treat a perchlorate concentration of 1000 ppb is ten times greater, at \$311 per acre-foot

#### **4.5.2.3 Sensitivity to Nitrate Concentrations**

The cost per acre-foot of water treated increases with increases in nitrate concentrations. For Redlands water, the impact of nitrate on cost can be analyzed, as shown in Figure 4-8.

Figure 4-8: Cost per Acre-Foot as a Function of Nitrate Concentration using Redlands Water.

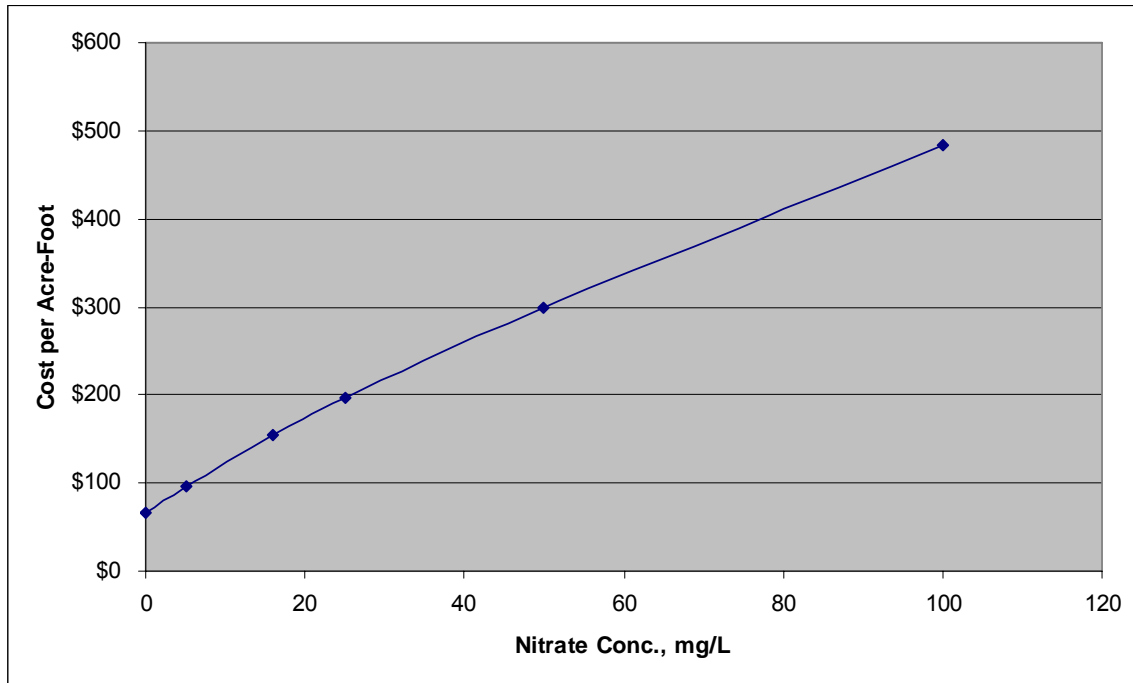


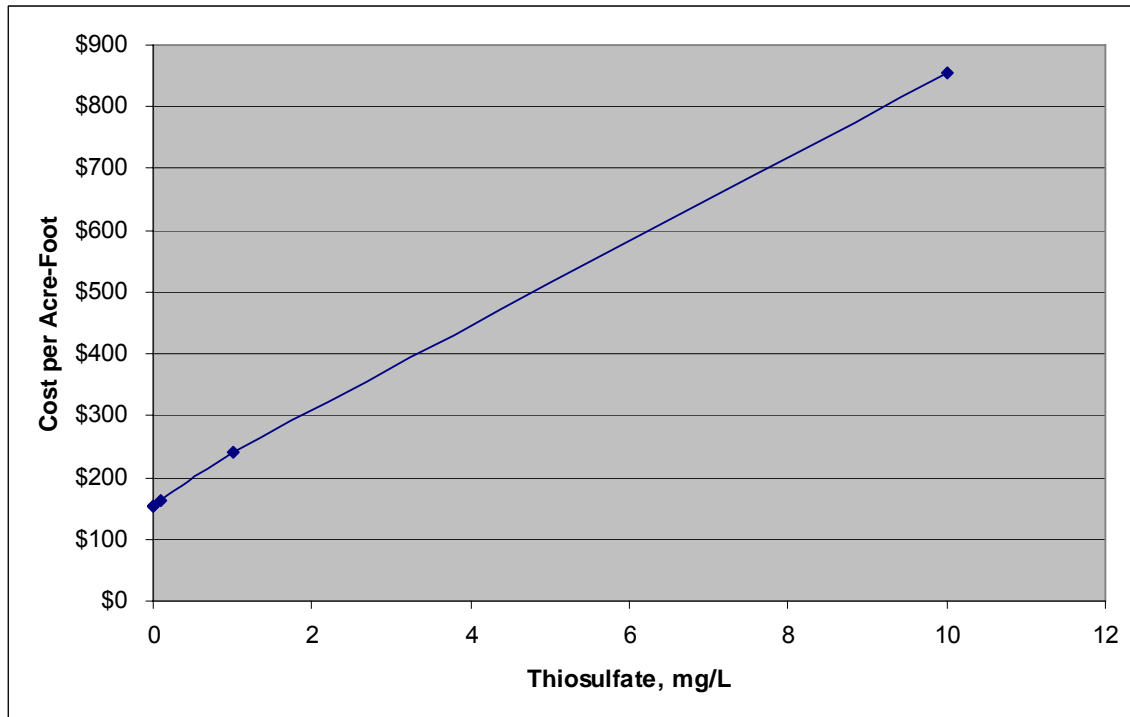
Figure 4-8 shows cost is highly sensitive to nitrate concentrations. An increase in nitrate concentration from 0 to 100 mg/L increases the costs over sevenfold.

#### **4.5.2.4 Sensitivity to Thiosulfate Concentrations**

The cost per acre-foot of water treated increases with thiosulfate concentration.

Assuming distilled de-ionized water with 75 ppb perchlorate concentration, the impact of thiosulfate on cost can be estimated, as shown in Figure 4-9.

Figure 4-9: Cost per Acre-Foot as a Function of Thiosulfate Concentration using Redlands Water.

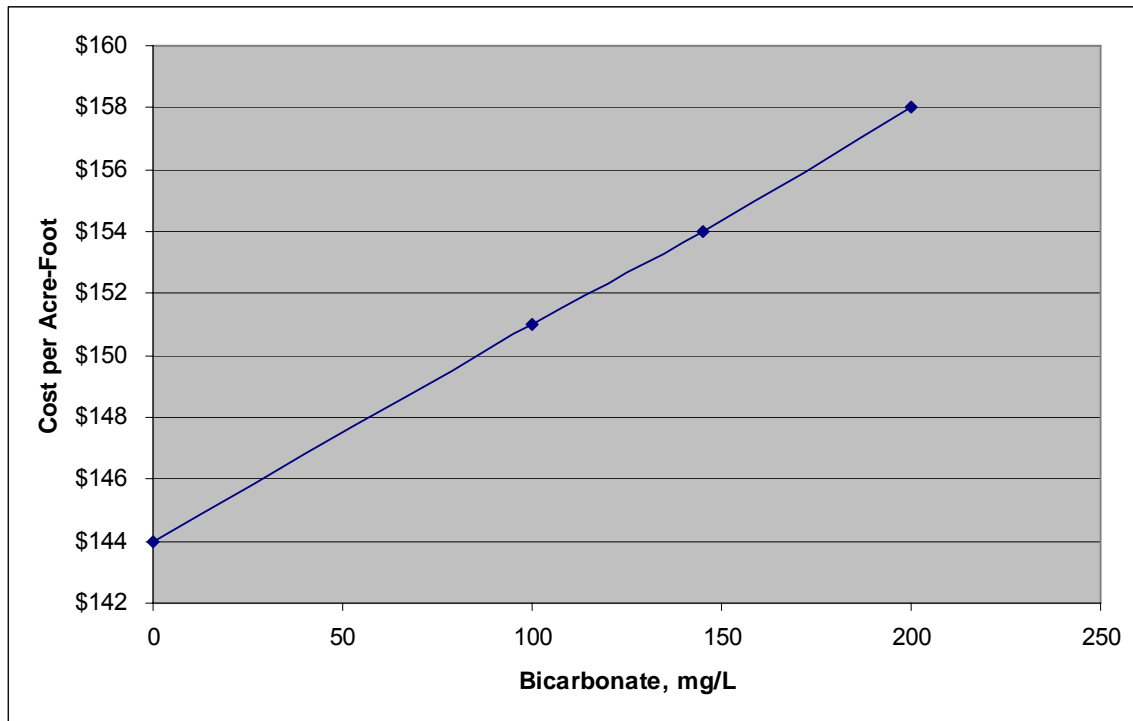


Cost is highly sensitive to thiosulfate concentration. Comparing Figures 4-8 and 4-9, we see that costs are much more sensitive to the presence of thiosulfate than to the presence of nitrate.

#### **4.5.2.5 Sensitivity to Bicarbonate Concentrations**

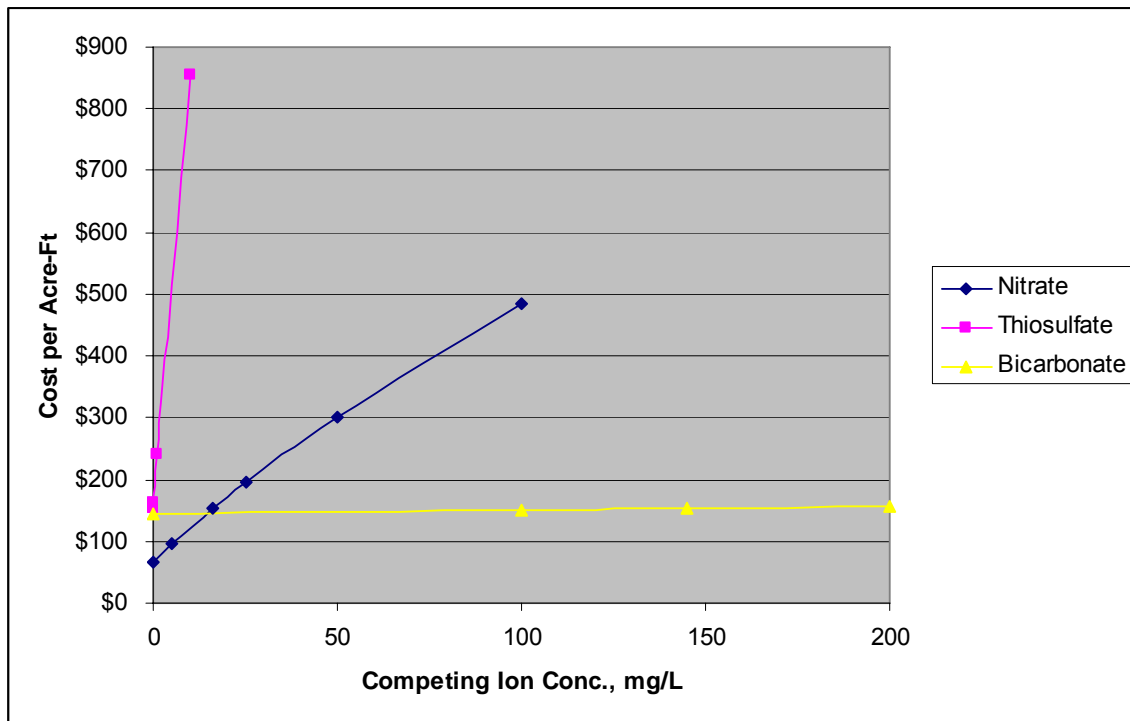
The cost per acre-foot of water treated increases with increases in bicarbonate concentrations. For Redlands water, the impact of bicarbonate can be analyzed, as shown in Table 4-8.

Figure 4-10: Cost per Acre-Foot as a Function of Bicarbonate Concentrations using Redlands Water.



As can be seen, bicarbonate concentration has only a small impact on overall cost, especially when compared to the impact of nitrate and thiosulfate. Cost vs all three competing ion concentrations are plotted on the same figure (Figure 4-11) for ease of comparison.

Figure 4-11: Cost per Acre-Foot vs Competing Ion Concentrations using Redlands Water.



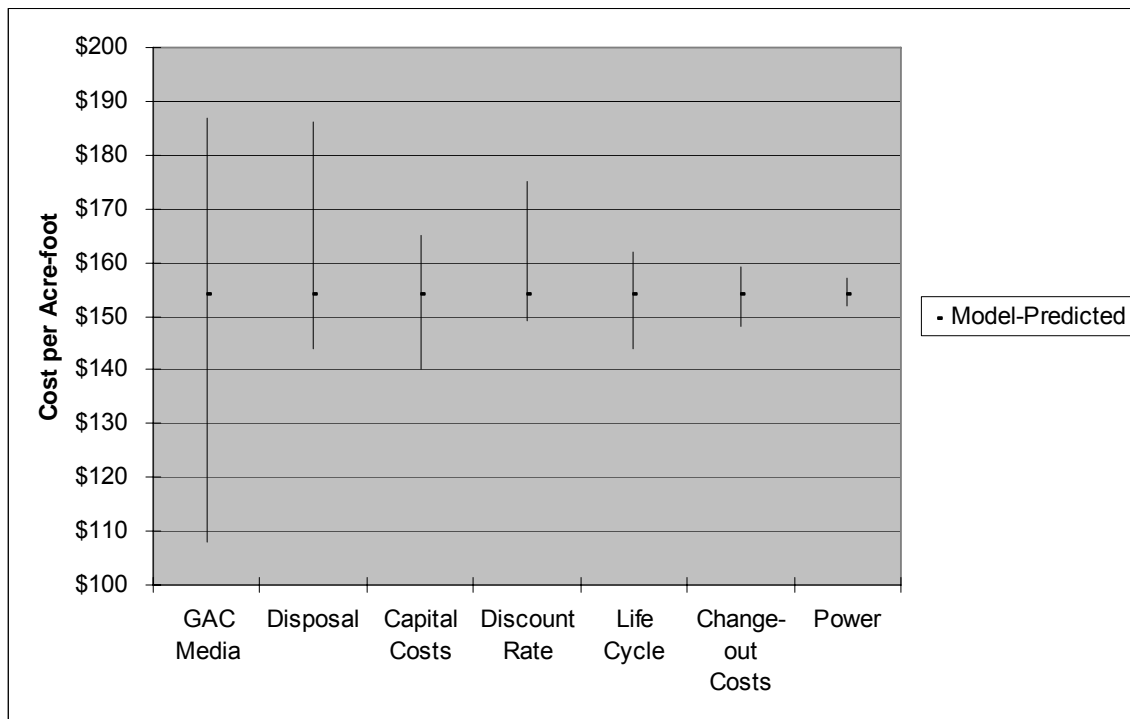
#### **4.5.3 Cost Sensitivity Analysis – Cost Assumptions**

Analyses of the sensitivity of costs to the assumptions noted in Chapter 3, Table 3-5, were conducted.

A tornado diagram was constructed to show how sensitive overall costs per acre-foot of water treated were to cost model assumptions (Figure 4-12). The diagrams can also be used to identify the most significant costs that should be minimized to improve overall cost performance. Each cost assumption is looked at individually. Redlands water was used to represent waters containing high concentrations of perchlorate or competing ions. On the diagram, the points on each vertical line represent the cost per acre foot calculated

based on the baseline cost assumptions in Table 3-5, a 15-year useful life, 3% discount rate and power costs of \$0.10 per kW-hr.

Figure 4-12: Tornado Sensitivity Diagram for Cost-based Assumptions (using Redlands data as a test case)



#### **4.5.3.1 Sensitivity to GAC Media Costs**

The cost per acre-foot of water treated increases with increases in GAC media costs. For Redlands water, the impact of GAC media costs was analyzed and the results are shown in Table 4-8. The baseline assumes a unit media cost of \$1.50 per pound of GAC. The lowest cost per acre-foot is identified by the cost model as the lowest cost obtained considering all the EBCTs and grain sizes included in the model's cost calculations.

Table 4-8: Cost per Acre-Foot versus GAC Media Cost for Redlands Water

GAC Media Costs \$ per lb	Lowest Cost \$/Acre-ft
\$0.80	\$108
\$1.00	\$121
\$1.25	\$138
\$1.50	\$154
\$1.75	\$170
\$2.00	\$187

GAC media costs have a significant impact on overall cost for waters containing high concentrations of perchlorate or competing ions, with an estimated cost range of over \$60 per acre-foot. Therefore, in developing a cost estimate, it is important to have a good estimate for GAC media costs.

#### **4.5.3.2 Sensitivity to Disposal Costs**

The cost per acre-foot of water treated increases with increases in disposal costs. For Redlands water, the impact of unit disposal costs was analyzed and the results are shown in Table 4-9. The baseline assumes disposal costs of \$10 per CF.

Table 4-9: Cost per Acre-Foot versus Unit Disposal Cost for Redlands Water

Disposal Costs \$ per CF	Lowest Cost \$/Acre-ft
\$5	\$144
\$10	\$154
\$15	\$165
\$20	\$175
\$25	\$186

Disposal costs have a significant impact on overall cost, with an estimated cost range of over \$40 per acre-foot. Therefore, in developing a cost estimate, it is important to have a good estimate for media disposal costs.

#### **4.5.3.3 Sensitivity to Capital Costs**

The cost per acre-foot of water treated increases with increases in capital costs. For Redlands water, the impact of unit capital costs was analyzed and the results are shown in Table 4-10. The baseline assumes initial capital costs of \$12 per pound of GAC.

Table 4-10: Cost per Acre-Foot versus Unit Capital Cost

Unit Capital Costs \$ per lb GAC	Lowest Cost \$/Acre-ft
\$6	\$140
\$8	\$146
\$12	\$154
\$15	\$160
\$18	\$165

Capital costs have a small but significant impact on overall cost. Capital costs are not expected to impact the model cost estimate for waters containing high concentrations of perchlorate or competing ions by more than \$15 per acre-foot.

#### **4.5.3.4 Sensitivity to the Discount Rate**

The cost per acre-foot of water treated increases with increases in the discount rate. For Redlands water, the impact of the discount rate was analyzed and results are shown in Table 4-11.



Table 4-11: Cost per Acre-Foot versus Discount Rate

Discount Rate %	Lowest Cost \$/Acre-ft
0%	\$149
3%	\$154
6%	\$159
10%	\$166
15%	\$175

The discount rate has a small but significant impact on the overall cost estimate.

Depending on the discount rate that's assumed, the overall cost estimate may vary by approximately \$25 per acre-foot of water treated.

#### **4.5.3.5 Sensitivity to Expected Useful Life**

The cost per acre-foot of water treated increases with decreases in the expected useful life. For Redlands water, the impact of expected useful life was analyzed and the results are shown in Table 4-12.

Table 4-12: Cost per Acre-Foot versus Useful Life

Life Cycle Years	Lowest Cost \$/Acre-ft
10	\$162
15	\$154
20	\$150
30	\$144

The expected useful life has a small but possibly significant impact on overall cost estimate. Depending on the useful life that's assumed, the overall cost estimate may vary by approximately \$18 per acre-foot of water treated.

#### **4.5.3.6 Sensitivity to Change-out Labor and Transport Costs**

The cost per acre-foot of water treated increases with increases in the cost for change-out labor and transport of the GAC media. For Redlands water, the impact of these service costs was analyzed and the results are shown in Table 4-13.

Table 4-13: Cost per Acre-Foot versus Service Costs

Service Costs \$ per bed	Lowest Cost \$/Acre-ft
\$2,500	\$148
\$3,500	\$151
\$5,000	\$154
\$6,000	\$157
\$7,500	\$159

The service costs incurred due to change-out labor have a small impact on the overall cost estimate. Depending on the service cost that's assumed, the overall cost estimate may vary by approximately \$11 per acre-foot of water treated.

#### **4.5.3.7 Sensitivity to Unit Power Costs**

The cost per acre-foot of water treated increases with increases in unit power costs. For Redlands water, the impact of unit power costs was analyzed and the results are shown in Table 4-14.

Table 4-14: Cost per Acre-Foot versus Unit Power Cost

Power Unit Cost \$ per kW-hr	Lowest Cost \$/Acre-ft
\$0	\$152
\$0.10	\$154
\$0.20	\$156
\$0.25	\$157

Unit power cost has the least impact on overall cost performance and the power cost assumption is not expected to affect the final decision on the technology's economic viability.

#### **4.5.4 Cost Sensitivity Analysis – Thermal Regeneration**

An examination of the tornado diagram in Figure 4-11 shows that significant cost savings may be gained by reducing GAC media and disposal costs. Both of these costs are factors in the calculation of annualized GAC replacement costs, the key factor that controls the overall T-GAC technology cost estimate (Table 4-4). Thus, it is apparent that significant cost savings may be achieved by reducing GAC replacement costs.

One way to reduce GAC replacement costs is through the use of thermal regeneration. Thermal regeneration of the GAC will reduce GAC replacement costs in two ways: 1.) By reducing the amount of GAC requiring disposal, and 2.) By reducing the amount of spent GAC that must be replaced, since the cost of regenerating GAC is less than the cost of purchasing new GAC. As noted in Section 3.5.3.5, thermally regenerated GAC has less adsorption capacity than fresh GAC, and a certain fraction of GAC is lost during the

regeneration process. To analyze the impact of thermal regeneration on overall costs, we apply the assumptions listed in Table 3-6 (reproduced here).

Table 3-6: Assumptions for Thermal Regeneration of GAC

Media Savings	\$0.30	per lb GAC
Disposal Costs	\$0	per lb GAC
Capacity Lost	15%	
Media Lost	5%	

Using these assumptions, the percent expected savings from assuming thermal regeneration is shown in Table 4-15.

Table 4-15. Expected Savings Gained by Thermal Regeneration of GAC to Treat Waters Analyzed in RSSCT Runs 1 through 11 (Appendix C)

RSSC T		CIO4-	Low	With	%
Run #	Water	ppb	\$/acre-ft	Regen.	Savings
1	Fontana Well 17C	7	\$217	\$189	12.9%
2	Fontana Well 17C	50	\$227	\$198	12.8%
3	Fontana Well 17C	500	\$334	\$287	14.1%
4	Fontana Well 17C, spiked 100 ppm nitrate	7	\$472	\$404	14.4%
5	Distilled Deionized	1000	\$311	\$268	13.8%
6	Distilled Deionized, spiked 10 ppb thiosulfate	1000	\$311	\$269	13.5%
7	Distilled Deionized, spiked 100 ppb thiosulfate	1000	\$318	\$274	13.8%
8	Distilled Deionized, spiked 1 ppm thiosulfate	1000	\$385	\$331	14.0%
9	Distilled Deionized, spiked 10 ppm thiosulfate	1000	\$963	\$814	15.5%
10	Redlands	75	\$154	\$135	12.3%
11	Massachusetts	5.6	\$23	\$22	4.3%

As can be seen from Table 4-15, the savings potential of utilizing thermal regeneration ranges from 4% to 15%, making it an attractive option that should be explored.

## **V. Conclusions and Recommendations**

### **5.1 Introduction**

The purpose of this chapter is to re-visit the original thesis objectives and determine the extent to which those objectives were met. The original thesis objectives were:

- Main Objective: Investigate to what extent data obtained from a small scale RSSCT can be applied to predict cost and performance, as well as to help prepare an initial design, of a full-scale T-GAC system to treat perchlorate-contaminated water.
- Sub-objectives:
  - Evaluate how well model predictions, which are based upon the RSSCT data, compare with actual technology performance.
  - Based on model simulations of technology cost and performance, determine under what conditions T-GAC is a viable treatment technology.

Furthermore, this chapter will also provide insight and recommendations on how to proceed with future research.

### **5.2 Conclusions**

Based upon the simulations presented in Chapter 4, particularly Figures 4-3 and 4-4, where calibrated model results are compared to RSSCT data, it appears the multi-component Freundlich model used in this study is capable of reproducing the effect of varying perchlorate and competing ion concentrations on T-GAC performance, where performance is quantified by the number of bed volumes that can be treated before breakthrough. However, the model has yet to be applied to predict RSSCT, and ultimately field, results where T-GAC is used to treat different waters.

The cost model provides indications of how various water quality and design parameters affect technology cost. However, while model cost predictions appear to be comparable to the costs of competing technologies, it is not possible to validate the accuracy of the cost model until real-world cost data are obtained.

### **5.2.1 Performance Modeling**

Overall, the Freundlich multi-component model using calibrated parameters performed well in reproducing the RSSCT breakthrough data characteristics, obtaining a mean error (difference between simulated and observed data) of 3.99% with a standard deviation of 6.41% over 11 RSSCT runs.

### **5.2.2 Cost Modeling**

The initial design used in this study to calculate costs is based upon the performance prediction of the Freundlich multi-component equation and the design assumptions listed in Section 3.4. The cost calculations are also only as good as the cost assumptions listed

in Table 3-5. The main factor that dominates the cost of treating waters containing high concentrations of perchlorate or competing ions is the cost associated with GAC replacement. For waters with low concentrations of perchlorate and competing ions, the capital cost, which is highly dependent on EBCT, dominates.

### **5.2.3 Model Prediction Compared to Actual Performance**

Since there are insufficient real-world cost and performance data at this time, this objective has not yet been explored and should be included in future research.

### **5.2.4 Conditions Where the T-GAC System is Viable**

The cost model estimates cost per acre-foot to treat perchlorate-contaminated water with a T-GAC treatment system. This cost can be compared to estimated IX costs to determine whether the T-GAC technology is a viable alternative to the conventional treatment technology. For waters containing low concentrations of perchlorate and competing ions, the T-GAC technology appears to be cost-effective. For waters containing high concentrations of perchlorate or competing ions, the cost effectiveness of the T-GAC technology is greatly reduced.

Thermal regeneration was explored as to its effects on overall costs. Since this process reduces the costs associated with GAC replacement, the potential savings may be significant and range from 4% to 15%.

## **5.3 Recommendations**



### **5.3.1 Model validation**

As noted above, the key question that still needs to be answered is how well does the model predict costs and performance of full-scale systems treating waters of various qualities? Data need to be obtained from full-scale systems to answer this important research question. Related to this is the question of how well do RSSCTs predict the performance of full-scale T-GAC systems? While RSSCTs have proved successful in predicting the performance of full-scale GAC systems, the only RSSCT study that was used to predict the performance of a pilot-scale T-GAC system (at Redlands, CA) overpredicted performance by 100%.

### **5.3.2 Improved performance model parameters**

As discussed in Chapter 3, only a very limited number of RSSCTs were used to determine the model parameters (the Freundlich equation  $K$  and  $1/n$ , as well as the competition coefficients). Future research should use the results of additional RSSCTs to improve the estimates of parameter values.

### **5.3.3 Expansion of performance model applicability**

Only nitrate, sulfate, thiosulfate, chloride, and bicarbonate were investigated for competition with perchlorate. Therefore, it is recommended that future studies examine the potential of other anions commonly found in drinking water to compete with perchlorate for adsorption sites. Also, the impact of dissolved organic matter (DOM)

was not considered in this study. Future research should examine the impact of DOM on overall performance.

#### **5.3.4 Performance model modification**

One questionable assumption of the Freundlich multi-component model (Equation 2-8) is that the values of the Freundlich parameters for perchlorate ( $K_i$  and  $1/n_i$ ) are constant, and independent of competing ion concentrations. For further research of this assumption, the Freundlich multi-component model could be modified to allow the Freundlich parameters to vary as a function of the competing ion concentrations.

#### **5.3.5 Examine Relation Between #BVs to Breakthrough and EBCT**

A key component of the performance model (and therefore, the cost estimates) was the assumed relationship between EBCT and #BVs to breakthrough. The relationship used in this study was based upon data from Redlands water (see Chapter 3, Figure 3-3). The question is raised as to whether the curve in Figure 3-3 is applicable for different water chemistries. Future work should examine how the relationship between EBCT and #BVs to breakthrough is affected by water chemistry (particularly, the concentrations of competing ions, and perhaps DOM concentration).

#### **5.3.6 Effect of Thermal Regeneration on Performance and Cost**

As noted in the conclusions, thermal regeneration has the potential to significantly reduce T-GAC technology costs. However, little is known about how effectively and

inexpensively T-GAC can be regenerated. Future research should study these questions, so results can be incorporated into the technology cost and performance model.

## Appendix A

### PSU Perchlorate Breakthrough Points

Table A-1. Observed #BVs to Breakthrough for Various RSSCT Runs Conducted by PSU

Water	ClO <sub>4</sub> - ppb	Sim 8x30 EBCT minutes	Tailoring Agent	Est. Observed Breakthrough (BVs)	Calculated x/m (mg/g)
Redlands	75	20	None	1000	0.156
Redlands	75	22	CTAC	34000	5.313
Redlands	75	15.52	CPC	33000	18.37
Redlands	75	8	CPC	27000	4.219
Redlands	75	8	Arquad T-50	27000	4.219
Redlands	75	7	Arquad 2C-75	23000	3.594
Distilled Deionized 0 ppb Thiosulfate	1000	20	CPC	14250	29.688
Distilled Deionized 10 ppb Thiosulfate	1000	20	CPC	13750	28.646
Distilled Deionized 100 ppb Thiosulfate	1000	20	CPC	12250	25.521
Distilled Deionized 1 ppm Thiosulfate	1000	20	CPC	11000	22.917
Distilled Deionized 10 ppm Thiosulfate	1000	20	CPC	4000	8.333
Fontana Well 17C	7	10	CPC	19000	0.277
Fontana Well 17C	50	10	CPC	18400	1.917
Fontana Well 17C	500	10	CPC	9300	9.688
Fontana Well 17C Spiked to 100 ppm NO <sub>3</sub>	7	10	CPC	8000	0.117
Fontana Well 17C Spiked to 50 ppm SO <sub>4</sub>	7	10	CPC	19000	0.277
Fontana Well 17C Spiked to 250 ppm SO <sub>4</sub>	7	10	CPC	19000	0.277
Massachusetts	5.6	5	CTAC	210000	2.450
Unknown Tap Water	800	20	Ultracarb	9000	15.000
Unknown Tap Water	800	20	Aquacarb	10000	16.667

## Appendix B

### Water Characteristics

Table B-1. Water Characteristics used in the RSSCT Runs Conducted by PSU

Water	ClO <sub>4</sub> - ppb	NO <sub>3</sub> - mg/l	NO <sub>2</sub> mg/l	Silicate mg/l	Thiosulfate mg/l	SO <sub>3</sub> - mg/l	SO <sub>4</sub> - mg/l	HS mg/l	H <sub>2</sub> S mg/l	Cl- mg/l	Bicarb mg/l	TDS mg/l
Redlands	75	15 - 25					30			7.2	145	
Fontana 17B	11 - 18	36					14			11	192	250
Fontana 17C	5 - 8.6	33					14			11	186	238
Massachusetts Distilled	5.6	0.4					6.9			7.6		
Deionized	1000				0 - 10							

## Appendix C

### Model RSSCT Runs

Table C-1. RSSCT Runs used in Determining Model Parameters

Run #	Water	ClO <sub>4</sub> -	#8 x 30 Mesh		NO <sub>3</sub> - mg/l	Thiosulfate mg/l	SO <sub>4</sub> - mg/l	Cl- mg/l	Bicarb mg/l	TDS mg/l	Est. Observed Breakthrough h (BVs)
			Sim EBCT minutes	% at Equilibrium							
1	Fontana Well 17C	7	10	88%	33	0	5	12	189	244	19000
2	Fontana Well 17C	50	10	88%	33	0	5	12	189	244	18400
3	Fontana Well 17C	500	10	88%	33	0	5	12	189	244	9300
4	Fontana Well 17C	7	10	88%	100	0	5	12	189	244	8000
5	Distilled Deionized	1000	20	95%	0	0	0	0	0	0	14250
6	Distilled Deionized	1000	20	95%	0	0.01	0	0	0	0	13750
7	Distilled Deionized	1000	20	95%	0	0.1	0	0	0	0	12250
8	Distilled Deionized	1000	20	95%	0	1	0	0	0	0	11000
9	Distilled Deionized	1000	20	95%	0	10	0	0	0	0	4000
10	Redlands	75	22	96%	16	0	30	7.2	145		34000
11	Massachusetts	5.6	5	35%	0.4	0	6.9	7.6			210,000

## Appendix D

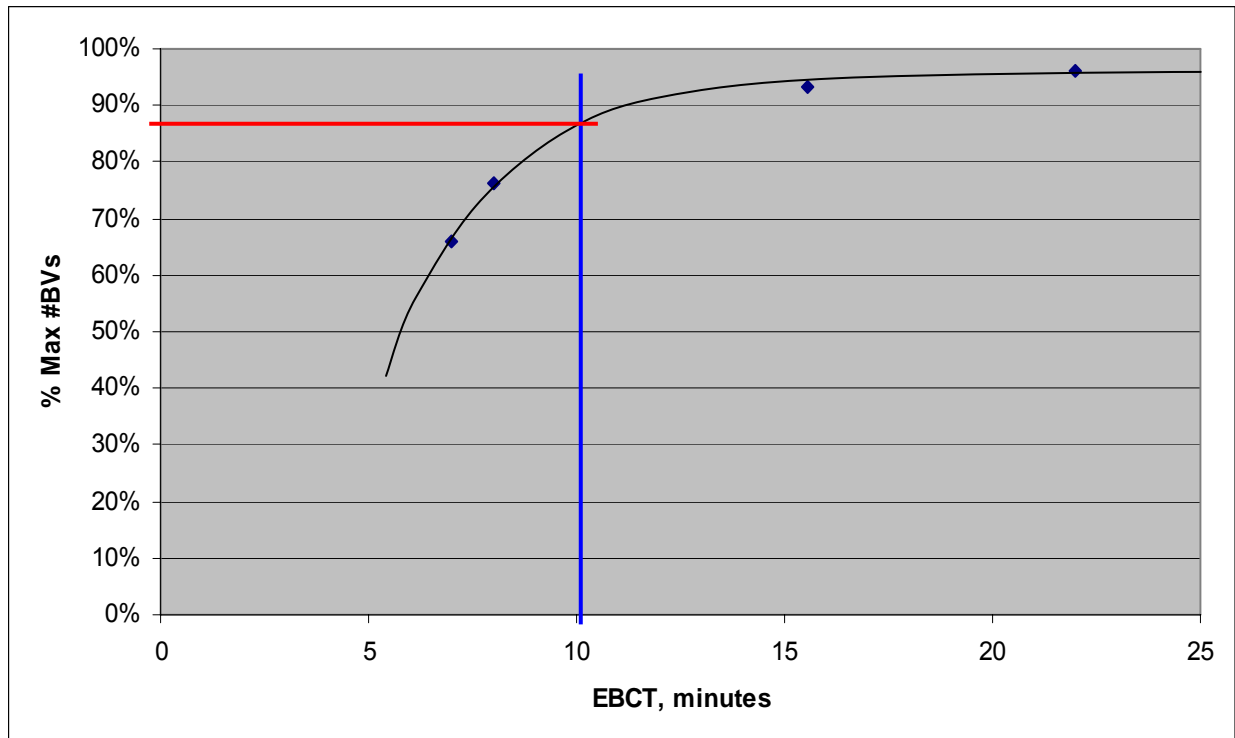
### **Achieved % Equilibrium Curve**

Table D-1. Formulation of EBCT Relationship Curve. Data obtained from Table A-1 for Redlands data

Redlands Water containing 75 ppb Perchlorate average

EBCT (min)	Breakthrough BVs	Calculated x/m (mg/g)	Estimated % $q_e$
Infinity		5.53	100%
22	34000	5.31	96%
15.56	33000	5.16	93%
8	27000	4.22	76%
7	23300	3.64	66%

Figure 3-3. EBCT Relationship Curve. Curve developed using Redlands data and Table D-1.



## Appendix E

### Design-Cost Screening Tool Walkthrough

#### Introduction

The objective of this thesis is to investigate how data obtained from a small scale RSSCT can be applied to predict cost, performance, and initial design of a full-scale T-GAC system to treat perchlorate-contaminated water. This appendix explains the design-cost screening tool. The tool was designed in MS Excel.

**Table E-1: User Input Screen. Input data seen here is used as the test case for all the following calculations.**

<u>User Input</u>		Quantity	Units
Design Flow Rate	=	5000	gpm
Expected Useful Life	=	15	years
Discount Rate (or IRR)	=	3%	per year
Power Costs =	=	\$0.10	per kW-hr
	=		
Thermal Regeneration Possible?		0	1 = yes, 0 = no
ClO <sub>4</sub> <sup>-</sup>	=	13	µg/l (ppb)
NO <sub>3</sub>	=	33	mg/l
NO <sub>2</sub>	=	0	mg/l
HAsO <sub>4</sub>	=	0	mg/l
Vanadium	=	0	mg/l
Silicate	=	0	mg/l
Thiosulfate	=	0	mg/l
SO <sub>3</sub>	=	0	mg/l
SO <sub>4</sub>	=	5	mg/l
HS	=	0	mg/l
Cl <sup>-</sup>	=	12	mg/l
Bicarb	=	189	mg/l
TDS	=	244	mg/l
NOM	=	2	mg/l



Table E-1 shows the screen for the user-inputted data for the water to be treated. Above data are used in the following calculations.

**Table E-2: Cost Assumptions**

<b>Cost Assumptions</b>		
Initial Capital Costs	\$12	per lb GAC
GAC media	\$1.50	per lb
Change-out Labor & Transport	\$5,000	per bed
Disposal	\$10	per CF

Table E-2 shows the cost assumptions used in the screening tool's calculations. The calculations are tied into the values shown in this box, and can be changed. Changing these values affects the results of the whole model. Economies-of-scale are not assumed for this model.

**Table E-3: Freundlich Competition Calculation Screen**

<b>Freundlich Competition Calculations</b>				
K =		30.3		
1/n =		0.153		
Chemistry	Competition Coefficient ( $a_{ClO4,i}$ )	Concentration mg/L ( $C_i$ )	$a_{ClO4,i} * C_i$	
ClO4-	1	0.013	0.013	
NO3	0.0169	33	0.5577	
NO2	0	0	0	
HAsO4	0	0	0	
Vanadium	0	0	0	
Silicate	0	0	0	
Thiosulfate	0.33212	0	0	
SO3	0	0	0	
SO4	0	5	0	
HS	0	0	0	
Cl-	0	12	0	
Bicarb	0.000226	189	0.042714	
TDS	0	244	0	
NOM	0	2	0	
<b>Sum</b>			<b>0.613414</b>	

Table E-3 contains the values for the Freundlich parameters K and 1/n, and the values for the competition coefficients as shown in section 4.2.4. As the screening tool is refined, these values can be changed.

**Table E-4: Flow Rate Conversions**

<b>Flow Rate Conversions</b>				
Q =	5000	gpm	1 acre =	43560 SF
	7.20	MGD		
	11.14	CFS		
	0.32	CMS		
	315.13	kg/s		
			<b>8065</b>	acre-ft per year

Table E-4 converts the flow rate from the input units of gpm to more useful forms used in the calculations of head loss, power requirements, etc., where:

Q = User Input Flow Rate (see Table E-1).

**Table E-5: Superficial Velocity, Total Number of Beds Calculations**

Standard Column Radius =	6	feet
As =	113	SF
n = Pump efficiency =	70%	
Single Column vs =	0.098	fps
Maximum vs =	0.048	fps
	divided into 2 beds per train, plus 50% virgin	
Number of Trains =	3	GAC per bed
Total # of beds =	6	
<b>Actual Superficial Velocity =</b>	<b>0.033</b>	<b>fps</b>

Table E-5 calculates the number of treatment trains and resulting total number of beds required to handle the given flow rate. This section assumes a standard 6-foot radius column design, a maximum superficial velocity of 0.048 fps based upon a maximum flow rate of 2400 gpm as noted in section 3.4.1, 2 beds per train each containing an extra 50% of virgin GAC to mitigate sloughing. Calculations are as follows:

$$As = \text{Area of Column} = \pi * 6^2 = 113 \text{ SF}$$

*vs* = superficial velocity

$$\text{Single Column } vs = \frac{Q(cfs)}{As}$$

$$\text{Number of Trains} = \frac{Q(gpm)}{2400 \text{ gpm}} \text{ rounded up to nearest whole number}$$

$$\text{Total \# of Beds} = 2 * \text{Number of Trains}$$

$$\text{Actual Superficial Velocity} = \frac{Q(cfs)}{As * \text{Number of Trains}}$$

**Table E-6: Reynolds Number, Head Loss Calculations**

<b>Reynolds #, Particle Size, Ergun headloss equation</b>							<b>Total</b>
<b>Sieve</b>	<b>Dia. (mm)</b>	<b>Diameter (in)</b>	<b>Diameter (ft)</b>	<b>Re<sub>lc</sub></b>	<b>Ergun 1st Term</b>	<b>Ergun 2nd Term</b>	<b>hL L</b>
200 x 400	0.059	0.00234	0.000195	10.14	23.836	4.701	28.537
8 x 30	1.187	0.04674	0.003895	202.86	0.060	0.235	0.295
12 x 40	0.840	0.03306	0.002755	143.51	0.119	0.332	0.451
20 x 40	0.594	0.02337	0.001948	101.44	0.238	0.470	0.708
20 x 50	0.499	0.01963	0.001636	85.21	0.338	0.560	0.897

Table E-6 converts the average particle diameters for each mesh size calculated from the geometric mean (per Chapter 3, section 3.4.6.2) and converts it to feet for purposes of the Ergun head loss equation. Using the superficial velocity (Table E-5), this section calculates the Reynolds Number using equation 2-14 and amount of head loss per unit length in accordance with the Ergun equation 2-15. Sphericity is assumed 0.6 and porosity is assumed 40% per Chapter 3, Section 3.4.6.1.

**Table E-7: Model-predicted # BVs Treated Before Breakthrough**

<b>Model Prediction</b>				
8 x 30 EBCT (minutes)	p (density) = % Achieved Equilibrium	479.895 g/L	Inhibited x/m	# BVs Treated
5	35%		0.209	7699
7	66%		0.393	14518
8	76%		0.453	16718
10	88%		0.524	19357
12	90%		0.536	19797
15	92%		0.548	20237
20	95%		0.566	20897

Table E-7 first

uses Table 3-4 to fill in the first two columns (EBCT and % Achieved Equilibrium), using equation 2-12 (assuming proportional diffusivity) to scale for each mesh size. The

% Achieved Equilibrium values were obtained from Table 3-4. The (x/m)-value for the Freundlich Multi-component system is calculated using equation 3-4. The # BVs treated is then calculated using equation 3-2. This is repeated for each mesh size (12 x 40, 20 x 40, and 20 x 50).

**Table E-8: Length per Bed, Head Loss, and Annual Power Costs**

(incl. V-GAC) Min BV (CF)	min L (ft)	L per Train (ft)	L per bed (ft)	(incl. V-GAC) hL (ft)	hL (m)	Power (watts)	Pwr Req'd kW-hrs	Annual Power Costs (\$)
5013	44.3	14.8	8.00	14.14	4.31	19037	166771	\$16,677
7018	62.1	20.7	11.00	19.45	5.93	26177	229311	\$22,931
8021	70.9	23.6	12.00	21.21	6.47	28556	250157	\$25,015
10026	88.6	29.5	15.00	26.52	8.08	35695	312696	\$31,269
12031	106.4	35.5	18.00	31.82	9.70	42835	375236	\$37,523
15039	133.0	44.3	23.00	40.66	12.39	54733	479468	\$47,946
20052	177.3	59.1	30.00	53.04	16.17	71391	625393	\$62,539

Table E-8 first calculates the minimum bed volume required based on the flow rate and EBCT, and accounts for the additional 50% virgin GAC required to prevent sloughing ( $BV = Q * EBCT * 1.5$ ). The required minimum length is then calculated by dividing the bed volume by a single column area ( $L = BV / A_s$ ). A required length per train is then calculated ( $L \text{ per train} = L / \text{Number of Trains}$ ). Since there are 2 beds in series per train, the length per train is divided by two and rounded up to the nearest whole number. Head loss (hL) is then calculated based on this new length ( $hL = \text{Total \# of beds} \times \text{Length per bed}$ ). Head loss is converted into meters, and Power is calculated according to equation 2-16, and divided by the pump efficiency (assumed 70%, Table E-5). Annual power required (kW-hrs) is found by multiplying Power by 8760 hours in a year. Annualized

power costs are calculated by multiplying by the user-inputted unit power costs on the user-input screen.

**Table E-9: Calculation of Initial Capital Costs**

<b>Capital Costs</b>			
(incl. V-GAC)	Total	Initial Capital Costs	Annualized
Bed Volume	lbs	Costs	Capital Costs
Actual (CF)	GAC	\$	\$
5429	162,317	\$1,947,806	\$163,161
7464	223,186	\$2,678,233	\$224,346
8143	243,476	\$2,921,709	\$244,742
10179	304,345	\$3,652,136	\$305,927
12215	365,214	\$4,382,563	\$367,112
15607	466,662	\$5,599,942	\$469,088
20358	608,689	\$7,304,272	\$611,854

Table E-9 first calculates the actual bed volume based on the length per bed (Table E-8).

The total weight (in pounds) of GAC is found by multiplying the bed volume by the GAC density. Initial capital costs are then calculated based on an assumed unit cost \$12 per lb GAC per section 3.4.2. The capital costs are then annualized based on user-inputted expected useful life, discount rate, and equation 2-17.

**Table E-10: Maintenance Costs**

T-GAC Bed Vol (gal)	Gallons H2O Treated	Days b/w Change- outs	Change - outs per yr	CF GAC per year	Annual Disposal Costs	lbs GAC per year	Annual GAC Costs
27073	208430917	29	12.6	68447	\$684,473	2046575	\$3,448,117
37225	540431593	75	4.9	36298	\$362,978	1085305	\$1,773,841
40609	678889274	94	3.9	31522	\$315,218	942502	\$1,529,883
50761	982602896	136	2.7	27223	\$272,234	813979	\$1,301,204
	120592173						
60914	6	167	2.2	26618	\$266,184	795890	\$1,259,213
	157514221						
77834	9	219	1.7	26040	\$260,397	778588	\$1,217,935
	212152898						
101523	1	295	1.2	25217	\$252,174	754001	\$1,168,164

Table E-10 calculates the annualized disposal costs of spent GAC and the annual GAC replenishment costs, based on the volume and weight of the GAC respectively. The amount (gallons) of water treated by one (total) bed volume is determined by the volume of T-GAC in one bed multiplied by the # BVs treated by one bed volume, known as the breakthrough bed volume, as calculated earlier (Table E-7). The number of days between change-outs of exhausted GAC (and replenishing with new GAC) is calculated as the volume of water (gallons) treated by one BV divided by the flow rate (gpd). The number of change-outs per year is simply calculated as 365 days per year divided by the number of days between change-outs.

The number of change-outs per year is multiplied by the total bed volume (GAC and T-GAC) to give the volume of GAC that must be disposed of per year (CF per year).

Annualized disposal costs are calculated after multiplying by the assumed unit costs per section 3.4.5.

An additional service charge must be made each time a bed is changed-out to account for labor and transportation costs. This is assumed a fixed per-bed cost per section 3.4.4.2, each time this service occurs. The service charge is calculated by multiplying the number of change-outs per year times the number of beds in the system times the fixed unit cost per change-out.

The volume of GAC that must be disposed of per year (CF per year) is multiplied by the GAC density (PCF) to give the weight per year of exhausted GAC (lbs per year).

Annualized GAC replenishment costs are calculated by multiplying the weight per year of exhausted GAC by the assumed unit costs per section 3.4.4.2, and adding the annualized service charge.

**Table E-11: Total Costs**

Grand Total \$ per year	Cost per Acre-ft
\$4,312,429	\$535
\$2,384,097	\$296
\$2,114,859	\$262
\$1,910,634	\$237
\$1,930,033	\$239
\$1,995,367	\$247
\$2,094,731	\$260

Table E-11 converts the total annualized cost to cost per acre-foot. The total annualized costs are simply calculated as the sum of the annualized power, capital, GAC disposal,



and GAC replenishment costs. The cost per acre-foot is calculated as the total annualized cost divided by the flow rate in acre-ft per year (see Table E-4).

## **Appendix F**

### **Performance Model Development Walkthrough**

#### **Introduction**

As presented in Chapter 1, the main objective of this thesis is to investigate how data obtained from a small-scale RSSCT can be applied to predict cost, performance, and initial design of a full-scale T-GAC system to treat perchlorate-contaminated water. This appendix explains the development of the performance prediction portion of the model. The performance model is based on equation 2-8, the Freundlich multi-component equation. The model was designed in MS Excel and uses Solver to determine parameter values from RSSCT data.

#### **Step 1: Determining RSSCT runs**

All data were from RSSCTs conducted at PSU. Data are tabulated in Appendix A, and summarized in Table F-1. Each water tested by PSU is labeled as an RSSCT run.

Table F-1. Summary of PSU RSSCT Data

RSSCT Run #	Water	Perchlorate Conc. (ppb)	Sim 8 x 30 EBCT (minutes )	Tailoring Agent	Observed Breakthrough (#BVs)
1	Redlands	75	20	None	1000
2	Redlands	75	22	CTAC	34000
3	Redlands	75	15.52	CPC	33000
4	Redlands	75	8	CPC	27000
5	Redlands	75	8	Arquad T-50	27000
6	Redlands	75	7	Arquad 2C-75	23000
7	Distilled Deionized 0 ppb Thiosulfate	1000	20	CPC	14250
8	Distilled Deionized 10 ppb Thiosulfate	1000	20	CPC	13750
9	Distilled Deionized 100 ppb Thiosulfate	1000	20	CPC	12250
10	Distilled Deionized 1 ppm Thiosulfate	1000	20	CPC	11000
11	Distilled Deionized 10 ppm Thiosulfate	1000	20	CPC	4000
12	Fontana Well 17C	7	10	CPC	19000
13	Fontana Well 17C	50	10	CPC	18400
14	Fontana Well 17C	500	10	CPC	9300
15	Fontana Well 17C Spiked to 100 ppm NO <sub>3</sub>	7	10	CPC	8000
16	Fontana Well 17C Spiked to 50 ppm SO <sub>4</sub>	7	10	CPC	19000
17	Fontana Well 17C Spiked to 250 ppm SO <sub>4</sub>	7	10	CPC	19000
18	Massachusetts	5.6	5	CTAC	210000
19	Unknown Tap Water	800	20	Ultracarb	9000
20	Unknown Tap Water	800	20	Aquacarb	10000

From this table, the number of RSSCT runs was paired down. Some of the above RSSCT runs were not used due to either redundancy or insufficient data on the water chemistry itself. For example, the RSSCT data exploring the effect of spiking SO<sub>4</sub><sup>-</sup> into Fontana water (RSSCT runs 16 and 17) showed that SO<sub>4</sub><sup>-</sup> had no observed effect on #BVs to

breakthrough. Thus, it was not necessary to analyze those RSSCT runs further, and they were eliminated from the model, although they were used to determine that  $\text{SO}_4^-$  did not compete with perchlorate and its competition coefficient was therefore assumed at zero. The spiked unknown tap water data (RSSCT runs 19 and 20) were eliminated as the water chemistry was unknown. RSSCT run 1 was eliminated because the RSSCT did not use T-GAC. The four Redlands water RSSCTs (RSSCT runs 2 through 6) were reduced to one RSSCT (RSSCT run 2) as the difference in performance of the different tailoring agents used in the four tests is assumed insignificant. It should be noted that RSSCT runs 2, 3, 4, and 6 were used in the development of the EBCT relationship curve in Chapter 3, section 3.3.1. The RSSCT runs used to develop the performance model are tabulated in Appendix C, and summarized in Table F-2.

Table F-2. Summary of RSSCT runs used to Develop Performance Model

RSSC T run #	Water	Perchlorate Conc. (ppb)	Sim 8 x 30 EBCT (minutes)	Tailorin g Agent	Observed Breakthroug h (#BVs)
1	Fontana Well 17C	7	10	CPC	19000
2	Fontana Well 17C	50	10	CPC	18400
3	Fontana Well 17C	500	10	CPC	9300
4	Fontana Well 17C Spiked to 100 ppm NO <sub>3</sub>	7	10	CPC	8000
5	Distilled Deionized, 0 ppb Thiosulfate	1000	20	CPC	14250
6	Distilled Deionized, 10 ppb Thiosulfate	1000	20	CPC	13750
7	Distilled Deionized, 100 ppb Thiosulfate	1000	20	CPC	12250
8	Distilled Deionized, 1 ppm Thiosulfate	1000	20	CPC	11000
9	Distilled Deionized, 10 ppm Thiosulfate	1000	20	CPC	4000
10	Redlands	75	22	CTAC	34000

### **Step 2: Determining Competing Ions**

The ions that were suspected of competing with perchlorate for adsorption sites and their concentrations for each of the RSSCT runs are listed in Appendix C. Some additional anions which might also compete with perchlorate were not considered for inclusion in the model equation due to insufficient data. Total dissolved solids and naturally-occurring organic matter (NOM) were deleted for this reason as well. Additionally, it has been shown that RSSCTs cannot reliably predict the fouling effect of dissolved organic carbon (DOC) as the presence of DOC has been shown to significantly decrease the adsorptive capacity of a pilot-scale column (Crittenden et al., 1991) when compared to RSSCT results. Sulfate was not considered a competing ion based on PSU's RSSCT results (see RSSCT runs 16 and 17 in Table F-1). Thus, competition coefficients (see equation 2-8) were only calculated for the following anions: nitrate, thiosulfate, chloride, and bicarbonate. However, the model is setup so that it can easily include other competing anions, should additional data become available.

### **Step 3: Determining Parameters for the Freundlich Multi-component Model**

We first must establish the values of K and 1/n to use in the Freundlich Multi-component Model (Equation 3-4). Recall equation 3-4:

$$(x/m)_{ClO_4} = (\% \text{ achieved } q_e) K_{ClO_4} C_{ClO_4} \left( \sum_{j=1}^k a_{ClO_4,j} C_j \right)^{(1/n - 1)} \quad (3-4)$$

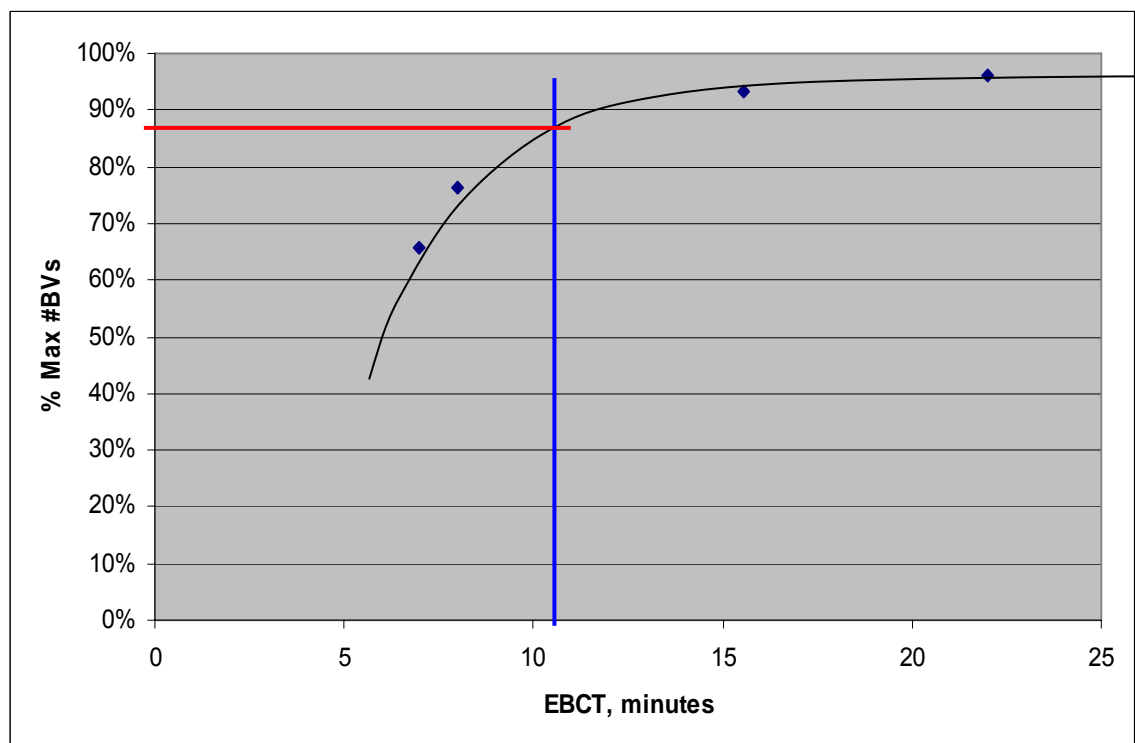
The parameter K is estimated at  $31.3 \text{ (mg/g)(L/mg)}^{1/n}$  as shown in section 4.2.1. The parameter  $1/n$  is initially estimated at 0.42, which is within the range reported in the literature (0.4 to 0.5) as discussed in section 2.4.1. The initial Freundlich parameters are as follows:

Table F-3. Initial Freundlich Parameters for Perchlorate

Perchlorate	K =	31.3
	$1/n =$	0.42

Next is finding the % achieved true equilibrium (or % achieved  $q_e$ ) based on the EBCT for each RSSCT run. The model used simulated EBCTs for the 8 x 30 mesh size, as noted in table F-2. Recall Figure 3-3, the EBCT relationship curve that was developed in Chapter 3, also simulated an 8 x 30 mesh size:

Figure 3-3: Plot of EBCT vs. % Maximum # BVs to Breakthrough for Redlands data



Using this curve, the EBCT for each RSSCT run is used to find its respective % achieved  $q_e$ , as shown in Table 3-4 reproduced below, which is input into the spreadsheet as shown in Table F-4 under the %  $q_e$  column.

Table 3-4. Effect of grain size on EBCT in scaling

<u>200 x 400</u> EBCT (minutes)	<u>20 x 50</u> EBCT (minutes)	<u>20 x 40</u> EBCT (minutes)	<u>12 x 40</u> EBCT (minutes)	<u>8 x 30</u> EBCT (minutes)	Percent Achieved $q_e$
0.25	2.10	2.5	3.54	5	35%
0.35	2.94	3.5	4.95	7	66%
0.4	3.36	4.0	5.66	8	76%
0.5	4.20	5.0	7.07	10	88%
0.6	5.04	6.0	8.49	12	90%
0.75	6.30	7.5	10.61	15	92%
1	8.40	10	14.15	20	95%
2	16.8	20	28.30	40	96%

Table F-4. Sample RSSCT run Inputs

		$C_j$ :	ClO <sub>4</sub> - mg/l	NO <sub>3</sub> - mg/l	Thiosulfat e mg/l	Cl- mg/l	Bicarb mg/l	Sum $a_j * C_j$
		$a_{j-}$	1	0	0	0	0	
		Constant						
RSSC T run	EBCT (min)	% $q_e$						
1	10	88%	0.007	33	0	12	189	
		$a_i * C_i =$	<u>0.007</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0.007</u>

The competition coefficients, noted in Table F-4 in the row containing “ $a_{j-}$ ,” for each suspected competing ion is initially set to zero, except for the perchlorate coefficient

which is kept constant at 1. The competition coefficient for each competing ion is then multiplied by their respective ion concentration, as noted in Table F-4 in the row containing “ $a_j * C_j$ ,” which in essence converts the competing ion concentrations in perchlorate concentration equivalents. The last column sums these “perchlorate equivalents,” thereby calculating the summation on the right-hand-side of equation 3-4:

This is accomplished for each RSSCT run. All the data needed to complete the calculation of equation 3-4 is now available.

#### **Step 4: Calculating (x/m) and Predicted # BVs to Breakthrough**

Once the “perchlorate equivalents” have been summed up in Table F-4, equation 3-4 is used to calculate  $x/m$  using the Freundlich parameter values in Table F-3 and the % achieved  $q_e$  values in Table F-4. This is shown in Table F-5. The model then calculates the #BV<sub>s</sub> treated before breakthrough is reached using:

$$\#BVs\ Treated = \frac{(x/m)(\rho_{GAC})}{(C_0)}$$

The observed #BV<sub>s</sub> treated to breakthrough for the data (see Table F-2) are then compared to the model-calculated #BV<sub>s</sub>, and the difference is calculated.

Table F-5. Calculation of Model-predicted x/m and # BVs Treated

Data Point	Sum $a_j * C_j$	x/m Model Calc	# BVs Treated Prediction	# BVs Treated Observed	Delta
1	0.633	0.284	19442	19000	442
2	0.676	1.916	18393	18400	7
3	1.126	12.455	11957	9300	2657
4	1.825	0.116	7954	8000	46
5	1.000	29.735	14273	14250	23
6	1.004	29.647	14231	13750	481
7	1.035	28.881	13863	12250	1613
8	1.351	23.064	11071	11000	71
9	4.510	8.333	4000	4000	0
10	0.390	4.993	31956	34000	2044
11	0.013	2.447	209,760	210,000	240

#### **Step 5: Setting up Solver Part 1: Competition Coefficients**

Solver iteratively finds the model parameters values that will minimize or maximize some objective function. Solver is set to stop when the objective function minimization or maximization is obtained (to within a user-defined tolerance) or when a user-defined maximum number of iterations occurs. In this study, Solver was set to 10000 iterations and 0.01% tolerance.



The unknown parameters in the Freundlich Multi-component equation are the competition coefficients. Therefore, Solver was set to find the values of the competition coefficients that minimized the objective function (see Table F-6). The objective function was defined to capture how well the model calculated experimental #BVs.

Table F-6. Identifying the Solver Independent Variables

		$C_i$ :	ClO <sub>4</sub> - mg/l	NO <sub>3</sub> - mg/l	Thiosulfat e mg/l	Cl- mg/l	Bicarb mg/l	Sum $a_j * C_j$
		$a_i =$	1	0	0	0	0	
		Constant						
RSSC T run	EBCT (min)	% $q_e$						
1	10	88%	0.007	33	0	12	189	
		$a_i * C_i =$	<u>0.007</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0.007</u>

Competition Coefficients that Solver will be set to change.

### Step 6: Setting up Solver Part 2: Objective Function

The difference between the observed #BVs and the model-calculated #BVs is calculated as delta shown in Table F-5. However, the sum of deltas was not used as the objective function because using the absolute value of delta would result in overweighting of those data that had a high #BVs. Thus, the percentage difference between the experimental #BVs and the model-calculated #BVs was used.

The percent difference between observed and predicted #BVs treated is calculated as the error, as shown in Table F-7. The Solver program was set up to minimize total error (shown in Table F-7) in terms of percent difference between predicted #BVs to

breakthrough and observed #BVs to breakthrough by changing the values for the competition coefficients (shown in Table F-6) until best fit competition coefficient values were found.

Table F-7. Calculating and Minimizing Error in Solver – include water for each RSSCT run

Data Point	Sum $a_j * C_j$	x/m Model Calc	# BVs Treated Prediction	# BVs Treated Observed	Delta	% Difference
1	0.633	0.284	19442	19000	442	2.27%
2	0.676	1.916	18393	18400	7	0.04%
3	1.126	12.455	11957	9300	2657	22.22%
4	1.825	0.116	7954	8000	46	0.57%
5	1.000	29.735	14273	14250	23	0.16%
6	1.004	29.647	14231	13750	481	3.38%
7	1.035	28.881	13863	12250	1613	11.64%
8	1.351	23.064	11071	11000	71	0.64%
9	4.510	8.333	4000	4000	0	0%
10	0.390	4.993	31956	34000	2044	6.01%
11	0.013	2.447	209,760	210,000	240	0.11%

Mean  
 4.28%

Variance  
 0.481%

Std Dev  
 6.94%

Total Error =

47.04%

Total Error that Solver is set to minimize

### **Step 7: Setting up Solver Part 3: Changing 1/n and K**

Recall the Freundlich parameters  $K$  and  $1/n$  were chosen based on literature values. To see how well these values compared with the values of  $K$  and  $1/n$  that would be calculated using the procedure described above, Solver was also allowed to vary  $K$  and  $1/n$ , along with the competition coefficients, in order to minimize the objective function. The results are reported in Chapter 4.

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